XVIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

ACTION OF SODIC ALCOHOLATES ON CHLORANIL. ACETALS DERIVED FROM SUBSTITUTED QUINONES.*

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Presented May 9, 1894.

INTRODUCTION.

DURING the study of the action of sodic alcoholates, sodium malonic ester, and similar reagents upon tribromdinitrobenzol and related substances,† carried on now for some years in this Laboratory, it has been observed repeatedly that one of the atoms of bromine is replaced by hydrogen. In all this work, however, the bromine replaced by hydrogen has stood in the meta position to two other atoms of bromine, and, as it was possible that this strange reaction depended on the symmetrical position of the three atoms of bromine, we undertook the study of a substance with a different constitution; and for this purpose selected chloranil, in which no one of the atoms of halogen is in the meta position to two others. While this substance was well fitted for our work, because the atoms of chlorine which it contains can be replaced with comparative ease, on the other hand the action of most of these reagents with it had been already studied by Stieglitz,‡ Ikuta,§ Kehrmann,‖ and others, and in no case could we find any mention of a direct replacement of chlorine by hydrogen; but still as it was

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† These Proceedings, XXIV. 1, 234, 256, 271, 288; XXV. 164; XXVII. 280; XXIX. 228.

‡ Am. Chem. Journ. XIII. 38.

§ These Proceedings, XXVI. 295.

‖ Journ. Prakt. Chem., [2.], XL. 365.

possible that the compounds formed by such a replacement might have been overlooked among the secondary products of some of these reactions, or might be formed under other conditions, we have carried through our experiments. In fact, one of them has proved that, when sodic methylate acts upon chloranil, a reduction takes place, but the hydrogen, instead of replacing chlorine, reduces part of the chloranil to the corresponding tetrachlorhydroquinone. The work with chloranil, therefore, did not throw light on the replacement of bromine by hydrogen in tribromdinitrobenzol, because of the presence of the two atoms of quinone oxygen, which seized upon the hydrogen before it could replace the halogen. In the mean time, however, our experiments have led to interesting results of another sort, which are described in this paper.

The action of potassic phenylate on chloranil was the first selected for study, and we found that, if the substances were mixed in the proportion of two molecules of the former to one of the latter, the product was dichlordiphenoxyquinone, $C_6Cl_2(OC_6H_5)_2O_2$, which melts at 243°, and gives a hydroquinone melting at 197°–198° when treated with reducing agents. With the object of replacing the two remaining atoms of chlorine we next treated the dichlordiphenoxyquinone with aniline, but instead of acting on the atoms of chlorine this reagent attacked the phenoxy groups, giving dichlordianilidoquinone and phenol, behaving in this respect in the same way as dichlordimethoxyquinone, which, Kehrmann* found, was converted by treatment with aniline into dichlordianilidoquinone. This action we found was the normal one for our substance; for example, sodium malonic ester gave with the dichlordiphenoxyquinone the dichlorquinonedimalonic ester melting at 132° discovered by Stieglitz †; and, strangely enough, this indirect method of preparing the substance gives a better yield than the direct action of sodium malonic ester on chloranil, for while Stieglitz by this latter method obtained only about 10 per cent, our yield was as high as 27 per cent. The beautiful bright blue sodium salt $C_6Cl_2O_2[CNa(COOC_2H_5)_2]_2$ was obtained, and analyzed; it is stable for a malonic ester salt. The "deep pure violet color, resembling exactly a concentrated solution of potassium permanganate," obtained by Stieglitz upon the addition of sodic hydrate to the substance, is due, according to our observations, to some decomposition of the salt brought about by an excess of the alkali. The solution of the pure salt has the full blue color of aniline blue.

* Journ. Prakt. Chem., [2.], XL. 370.   † Am. Chem. Journ., XIII. 38.

Sodic methylate acted on the dichlordiphenoxyquinone like the two reagents already mentioned; that is, the two phenoxy groups were replaced by two methoxy groups; but this action was followed by another and more interesting one, which formed a crystalline salt, appearing as a precipitate, if the amount of methylalcohol used as the solvent was small. Upon the addition of an acid to this salt a white substance was set free having the following formula:

$$C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2.$$
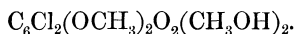
The sodium salt was also analyzed, and proved to have the formula

$$C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2.$$

The two molecules of methyl alcohol appearing in this last formula are evidently only alcohol of crystallization, as they could be easily driven off by heat. The corresponding ethyl compound,

$$C_6Cl_2(OC_2H_5)_2O_2(C_2H_5OH)_2,$$
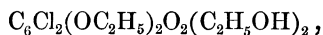
and the methylethyl compound,

$$C_6Cl_2(OCH_3)_2O_2(C_2H_5OH)_2,$$
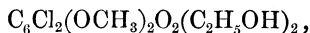
were also obtained, and resembled the methyl compound most closely in properties. In considering the way in which the two molecules of methyl alcohol (or sodic methylate) are attached to the molecule of $C_6Cl_2(OCH_3)_2O_2$, only two formulas seemed to us sufficiently probable to merit discussion. In the first of these (I.) the double bonds of the benzol ring are broken, and the radicals NaO and CH_3 added directly to the ring after the manner of the bromine and chlorine addition compounds discovered by Nef.[*] In the second (II.) the NaO and CH_3 have been added to the two carbonyl groups of the quinone, transforming it into a substance closely related to the acetals.
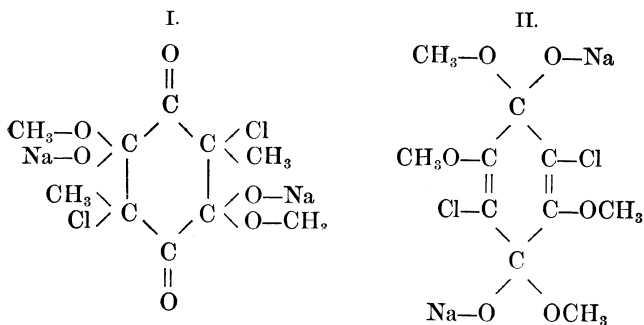
* Am. Chem. Journ., XII. 483; XIII. 422.

The various isomeric forms of Formula I. need not be considered, as the arguments which follow will apply as well to them as to this one. From the properties of the substance, it is not possible to decide between these formulas. It is white, like Nef's bromine addition products, but an acetal like Formula II. would also probably be white, as the colors of chloranil and its derivatives undoubtedly depend on the fact that they are quinones, and in such an acetal as this the quinone nature is obliterated. Its most striking property is the ease with which the free substance loses the two additional molecules of methyl alcohol, since it passes into dichlordimethoxyquinone when heated to temperatures from 160° to 195°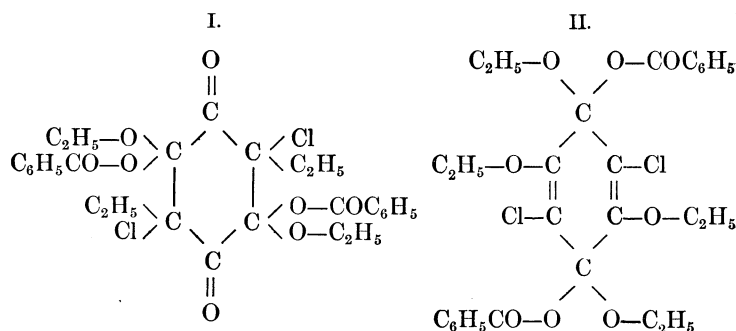; the same change is brought about by dilute sulphuric or hydrochloric acid, slowly in the cold, more rapidly when the mixture is warmed gently. While this instability is in harmony with the second formula given above, it is hard to connect it with the first, as it seems improbable that a methyl group attached directly to the benzol ring, as in Formula I., could be so easily removed. It must be remembered in this connection, however, that Stieglitz * by treating the dichlorquinonedimalonic ester with dilute sodic hydrate in the cold obtained parachlorhydroxyquinone, $C_6ClOHH_2O_2$. As in this case carbon atoms attached to the quinone ring were removed by a dilute alkali in a few minutes, it might be that the methyl group in Formula I. could be removed under the conditions observed by us. The objection to Formula I. mentioned above might also be met by substituting for it one in which the radicals added were Na and CH_3O instead of NaO and CH_3 as in that formula, but such an addition seems to us at the best improbable. It should be remarked here that Nef's bromine addition compounds were decomposed with the utmost ease by alkalies, but were very stable in contact with acids, being crystallized from strong nitric acid ; our substances show just the opposite behavior, as they are rather remarkably stable toward alkalies ; but this difference might be due to the difference in the nature of the radicals added (Br_2 in one case, NaO and CH_3 in the other) rather than to a difference in the structure of the compounds.

Since, as explained above, the properties of our new substance were not sufficient to prove the correctness of one or the other of the two formulas proposed, we next turned our attention to some experiments with derivatives of this substance, or rather of the corresponding ethyl compound, which have settled the question conclusively.

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* Am. Chem. Journ., XIII. 38.

To obtain material for this work, which would be possessed of the requisite stability, we replaced the sodium in the salt of our substance with the benzoyl radical forming a compound which must have one of the following formulas, according as one or the other hypothesis about these substances is adopted.

I.

$$
\begin{array}{c}
O \\
\| \\
C
\end{array}
$$

$$
\begin{array}{c}
C_2H_5-O \\
C_6H_5CO-O
\end{array}
\Big\rangle C
\Big/ \overset{\displaystyle}{\diagdown} C
\Big\langle
\begin{array}{c}
Cl \\
C_2H_5
\end{array}
$$

$$
\begin{array}{c}
C_2H_5 \\
Cl
\end{array}
\Big\rangle C
\diagdown \Big/ C
\Big\langle
\begin{array}{c}
O-COC_6H_5 \\
O-C_2H_5
\end{array}
$$

$$
\begin{array}{c}
C \\
\| \\
O
\end{array}
$$

II.

$$
\begin{array}{cc}
C_2H_5-O & O-COC_6H_5 \\
\diagdown & \diagup \\
& C \\
\diagup & \diagdown
\end{array}
$$

$$
\begin{array}{cc}
C_2H_5-O-C & C-Cl \\
\| & \| \\
Cl-C & C-O-C_2H_5 \\
\diagdown & \diagup \\
& C \\
\diagup & \diagdown
\end{array}
$$

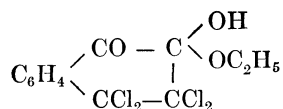$$
C_6H_5CO-O \qquad O-C_2H_5
$$

In Formula I. the carbonyl groups are unaffected, and the body should therefore retain the properties of a diketone. In Formula II., on the other hand, the carbonyl groups having been transformed into acetal groups, the body should have lost its diketone nature. Accordingly, a substance constituted like Formula I. should be converted by reducing agents into a substance containing secondary hydroxyl groups, and by the chloride of hydroxylamine into a mono or dioxime. Upon treating our substance with zinc dust and glacial acetic acid, (which we have found the most efficient agent for converting quinones into hydroquinones,) it remained entirely unaltered, and the same result was obtained when we tried to act on it with chloride of hydroxylamine. The substance therefore shows neither of these characteristic reactions of the diketones and must be constituted according to Formula II. To meet the not overstrong objection that the diketone properties of the substance might have been weakened or destroyed by the presence of radicals attached to the ring, we treated dichlordiethoxyquinone with the reducing mixture, and also with chloride of hydroxylamine, and in both cases obtained a satisfactory quinone reaction. We tried also to determine the constitution of our substance in another way. This consisted in making the dichlordiethoxyquinone tetraethylacetal $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$ by replacing the sodium in the sodium salt $C_6Cl_2(OC_2H_5)_2(ONa)_2(OC_2H_5)_2$ by ethyl, and then treating this dissolved in chloroform with bromine in the hope of making an addition product similar to those of Nef. The

result of this experiment was negative, as no bromine was taken up, but this cannot be accepted as an argument against Formula II., since Nef[*] found that dichlordiethoxyquinone itself gives no addition compound with bromine, — a result which we can confirm. The failure of the tetraethylacetal to form addition compounds must be ascribed, therefore, to the presence of the two atoms of chlorine and two ethoxy groups attached to the quinone ring, rather than to the absence of double bonds.

It is perhaps worth noting that the formation of these hemiacetals is easily explained by the diketo formula of quinone, but cannot be brought into harmony with the peroxide formula, so far as we can find. Our work, therefore, would have been of value in determining the constitution of quinone, if it had been done before this question was finally settled by Nef's proof of the diketo constitution through his work on the action of bromine on argentic chloranilate.[†]

Since, as we have just proved, our new substance has the two molecules of methyl alcohol attached to the two carbonyl groups of the dichlordimethoxyquinone, it belongs to the class of acetals, and we propose to call it and similarly constituted bodies hemiacetals, because only half of the hydrogen in the hypothetical mother group of the acetals $=C=(OH)_2$ has been replaced by the organic radical. Such hemiacetals are not especially uncommon, the most familiar examples being the alcoholates of ordinary chloral and of butylchloral. Jacobsen,[‡] and later Renard,[§] claimed that they obtained the corresponding compound of acetaldehyd $CH_3CH(OH)(OC_2H_5)$, but do not agree in regard to its boiling point, and apparently assign to it a much greater stability than would be expected in such a substance. Without multiplying examples, we pass at once to some compounds more nearly related to ours, recently obtained by Zincke with some of his scholars. Zincke and Arnst[‖] by the action of alcohol on tetrachlordiketohydronaphthalin have obtained a compound,

$$C_6H_4 \diagdown \diagup \begin{matrix} CO - C \diagup \diagdown \begin{matrix} OH \\ OC_2H_5 \end{matrix} \\ | \\ CCl_2 - CCl_2 \end{matrix}$$

which is tolerably stable in the cold, but decomposed by heat, like our hemiacetal. The corresponding para compound formed no such deriv-
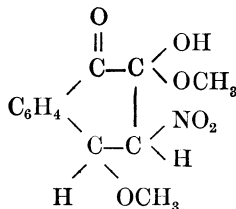
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[*] Am. Chem. Journ., XI. 20, 24. [§] Ber. d. ch. G., VIII. 132.

[†] Ibid., XII. 466. [‖] Ann. Chem., CCLXVII. 319.

[‡] Ber. d. ch. G., IV. 215.

ative.   Zincke and Neumann,[*] by the action of alcohol on nitro-β-naphthoquinone, obtained a substance the formula of which was made out as follows : —

$$C_6H_4 \underset{\underset{H}{\diagdown}\ \underset{OCH_3}{}}{\overset{\overset{O}{\underset{\diagup}{\parallel}}}{\diagup}} \begin{matrix} C-C\diagup^{OH}_{\diagdown OCH_3} \\ | \quad \diagup^{NO_2} \\ C-C\diagdown_H \end{matrix}$$

Still later, Zincke and Schaum [†] have made similar compounds from the isomeric heptachlorketotetrahydrobenzols by the action of sodic methylate.   Although Zincke's work shows that ring ketones, ortho-diketones, and orthoquinones are capable of forming such hemiacetals, so far as we can find our compound is the first of this class to be made from a paraquinone, and the compound of Zincke's which approaches most nearly to it, the orthoquinone derivative, differs from it strikingly, for, whereas in our compound both carbonyls are converted into hemi-acetal groups, in Zincke and Neumann's only one of the carbonyl groups is thus affected, and at the same time a molecule of sodic methylate is added to the ring by the breaking of a double bond.   It should be mentioned here that J. U. Nef [‡] has assumed the formation of addition products of water or hydrochloric acid with the carbonyls of quinone in explaining the formation of hydroquinone by the action of water,[§] or substituted hydroquinones by the action of hydrochloric acid on quinone ; [‖] but he supposes that these intermediate products break up immediately, and none of them have been isolated.

The discovery of the hemiacetals of the quinones has suggested to us a possible explanation of the constitution of quinhydrone and the bodies related to it.   The most important of these substances are quinhydrone, formed from one molecule of quinone and one of hydro-quinone ; resorcinequinone, from one molecule of quinone and one of resorcine ; phenoquinone, from one molecule of quinone and two of phenol ; and quinhydronedimethylether, from one molecule of quinone and two of the monomethylether of hydroquinone.   The state of our

* Ann. Chem., CCLXXVIII. 173.

† Ber. d. ch. G., XXVII. 537.

‡ Am. Chem. Journ., XIII. 427 ; Ann. Chem., CCLXX. 323 ; Clark, Am. Chem. Journ., XIV. 553.

§ Hesse, Ann. Chem., CCXX. 367 ; Ciamician, Gazz. Chim., XVI. 111.

‖ Levy, Schultz, Ann. Chem., CCX. 133 ; Sarauw, Ibid., CCIX. 93.

knowledge of the constitution of these substances is described in the following quotation from a paper on this subject by Nietzki : * " Aus vorstehenden Versuchen scheint hervorzugehen, dass das Chinhydron, das Chinonresorcin, blosse Additionsproducte des Chinons mit phenolartigen Körpern sind, und zwar scheint hierbei die Zahl der in letzteren enthaltenen freien Hydroxyle stets den beiden Chinonsauerstoffen zu entsprechen.   Eine Formel im Sinne der Structurtheorie lässt sich für diese Körper wohl augenblicklich kaum aufstellen, denn die von Kekulé für das Chinhydron vorgeschlagene Structurformel

$$C_6H_4 \underset{\diagdown O - O \diagup}{\overset{\diagup OH \; HO \diagdown}{}} H_4C_6$$
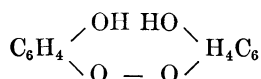
lässt sich für die Verbindungen des Chinons mit einwerthigen Phenolen nicht mehr anwenden.   Aus dem von O. Hesse beobachteten Verhalten des Chinhydrons gegen Essigsäureanhydrid scheint jedoch hervorzugehen dass das Chinhydron keine freien Hydroxyle enthält.   Auch das von Wichelhaus beobachtete Verhalten des Monomethylhydrochinons spricht dafür, dass Substitutionsproducte des Chinhydrons in den Hydroxylgruppen nicht existiren."

It appears from this quotation that there is no satisfactory theory for the constitution of these compounds, since the statement that they are addition products amounts to saying that we have no theory on the subject.   We would, therefore, advance the following theory in regard to the constitution of these bodies : that they are hemiacetals similar to those described in this paper ; in phenoquinone the phenol, in quinhydrone the hydroquinone, taking the place of the methyl or ethyl alcohol, which is added to the substituted quinones in our new substances. On this theory the graphical formulas of phenoquinone and quinhydrone would be written as follows : —
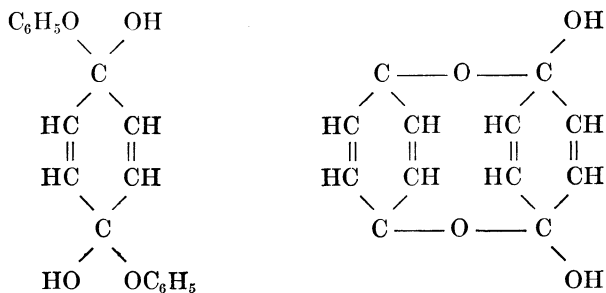
The principal arguments in favor of this theory are the following. It requires the union of one molecule of quinone with one molecule of a diatomic phenol such as hydroquinone or resorcine, but with two of a monatomic phenol like common phenol or monomethylhydroquinone, and is in this respect in accordance with the facts. Such substances would not be formed when the hydroxyl groups of the phenols had been converted into alkyloxyl groups, and dimethyl hydroquinone has no action on quinone. The products should be unstable, as we have found that the stability of our new hemiacetals depends on the number and strength of the negative radicals attached to the quinone ring, and in these cases, where there are no negative radicals, we should expect a very slight stability. As a matter of fact, these substances are not only decomposed by acids or alkalies, but quinhydrone even by solution in neutral solvents.* The action of acetic anhydride giving diacetylhydroquinone and quinone,† which is brought up by Nietzki as a proof of the absence of free hydroxyl, is really in accordance with our theory, as our dimethyl hemiacetal with acetic anhydride gave methyl acetate and the quinone from which the hemiacetal was derived. All these observed facts, therefore, are in harmony with our theory. Against it is the marked color of all this quinhydrone group, whereas our hemiacetals are colorless. This may be due, however, to the difference in the nature of the radicals attached to the carbonyl groups, our hemiacetals containing methyl or ethyl, the quinhydrone group aromatic radicals, which might well give more colored compounds. It may be remarked in this connection, that, while the methyl or ethyl ether of resorcine is colorless, the simple resorcine ether itself is reddish brown. An attempt will be made next year to find other parallel cases. Another objection to our theory is, that no salts have been obtained from phenoquinone, whereas the substance, according to our formula, contains two free hydroxyls. Wichelhaus, who states that he obtained no salts of it, adds that the substance turns blue when treated with alkalies; this may indicate the formation of a salt not yet isolated. We have attempted to test our theory by experiment in this direction, but so far with little result. By treating phenoquinone with sodic ethylate, not in excess, we obtained a green salt; but, as much phenol was found in the filtrate, we are inclined to consider this salt at present rather a product of the action of sodic ethylate on the quinone formed by the decomposition, than a salt of the phenoquinone

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* Clark, Am. Chem. Journ., XIV. 574.

† Hesse, Ann. Chem., CC. 248.

itself.   If this interpretation of the observation is true, it has no bear-
ing on our theory, as it shows only that the phenoquinone is easily
decomposed by alkalies, this decomposition taking place before it had
time to form a salt.   We then tried the action of sodic phenylate on
quinone, as according to our theory this should act as well, or even
better than free phenol, and we have succeeded in getting an action in
this case, a strongly colored product being formed ; but these experi-
ments were undertaken so late in the year that we had no time to
isolate this substance for study.   We should add that in the action
of potassic phenylate on chloranil, described at the beginning of the
experimental part of this paper, there are strong indications of the
formation of a diphenylhemiacetal, as the liquid took on a blue-black
color in the cold, which upon heating changed to the red of the di-
chlordiphenoxyquinone.   The isolation of this hemiacetal, if possible,
will throw a great deal of light upon our theory of the nature of
phenoquinone.   All these lines of work will be taken up in this Labo-
ratory during the next academic year, and we hope that by means of
these experiments we shall succeed in testing thoroughly our theory
that quinhydrone and phenoquinone are hemiacetals of quinone.   The
curious addition compounds of the nitranilines and quinones [*] will also
be considered in this connection.

The dichlordimethoxyquinone dimethylhemiacetal

$$C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2,$$
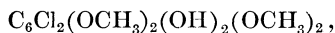
although most conveniently made from the dichlordiphenoxyquinone
by the action of sodic methylate, can also be obtained by the action of
the same reagent on dichlordimethoxyquinone, or even on chloranil.
In this last case the first product is a green sodium salt, which by treat-
ment with water yields the sodium salt of the hemiacetal and the
tetrachlorhydroquinone, mentioned at the beginning of this paper.
With sodic ethylate and chloranil we have not succeeded in obtaining
the corresponding ethyl compound ; it may be, however, that this
result was due to not finding the proper conditions for the reaction.

The dichlordiethoxyquinone tetraethylacetal

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4,$$
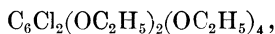
alluded to in the discussion of the constitution of the hemiacetals, was
made by the action of ethyliodide in the cold on the silver salt of the
corresponding hemiacetal.   The yield was exceedingly small, most of

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[*] Hebebrand, Ber. d. ch. G., XV. 1973; Niemayer, Ann. Chem., CCXXVIII.
332.

the hemiacetal dropping back to dichlordiethoxyquinone. Its proper-
ties were strangely unlike those of the corresponding hemiacetal, for
whereas the dichlordiethoxyquinone hemiacetal was essentially in-
soluble in all solvents, the tetraethylacetal was so easily soluble in all
the common solvents except water, that it was hard to crystallize it
from any of them. The most striking property of the hemiacetal was
its instability, since it gave up ethyl alcohol at temperatures from
140° to 143°, becoming converted into the dichlordiethoxyquinone
(melting at 104°–105°) ; the tetraethylacetal, on the other hand, melts
without decomposition at 101°–102°, and from 205° to 275° sublimes
apparently unaltered. The hemiacetal is converted into dichlordie-
thoxyquinone when treated with acids, even more easily than by heat,
dilute sulphuric or hydrochloric acid acting on it slowly even in the
cold, rapidly when warmed. This is its most marked property ; in
fact, it is so susceptible to the action of acids that in our earlier prep-
arations we obtained a considerable amount of dichlordiethoxyquinone
by drying the hemiacetal at ordinary temperatures, when it had not
been washed enough to remove the last traces of acid. In order to
bring about a similar decomposition of the tetraethylacetal it is neces-
sary to boil it with sulphuric acid of specific gravity 1.44. A more
dilute acid does not act upon it, and even this rather strong sulphuric
acid has no action in the cold. With alkalies the hemiacetal forms
crystalline salts, which are comparatively stable, since they dissolve
in water without decomposition, and can be kept in the dry state for
a moderate length of time. The stability of the substance toward
alkalies is in marked contrast to its behavior with acids, as it is neces-
sary actually to boil it with sodic hydrate in order to convert it into
chloranilic acid. The tetraethylacetal can of course form no salts, as
it contains no hydroxyl. It is even more stable toward alkalies than
the hemiacetal, as sodic hydrate even when boiling or mixed with
alcohol does not decompose it. Finally the hemiacetal is amorphous,
the acetal crystallizes finely, so that almost the only property which
they have in common is their white color. The salts of the hemia-
cetals which are not derived from the alkalies are insoluble in water.

The dichlordiethoxyquinone dibenzoyldiethylacetal,

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2,$$
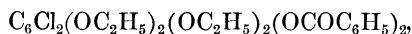
also mentioned in the discussion of the constitution of the hemiacetals,
was made by the action of benzoyl chloride on the sodium salt of the
corresponding hemiacetal suspended in alcohol. In this case the yield
is good, about 66 per cent of the theoretical, so that this substance is

much more accessible than the tetraethylacetal; it crystallizes well, and melts at 170°. It is a curious fact that none of the benzoyl compound is formed, if the sodium or silver salt of the hemiacetal is suspended in ether instead of alcohol, and treated with benzoyl-chloride. In order to obtain this benzoyl compound, therefore, it is essential to use alcohol as the diluent. The reaction with ether is apparently the same as that which occurs when the free hemiacetal or its sodium salt is heated to 100° with benzoylchloride, the products in this case being dichlordiethoxyquinone and ethyl benzoate.

When the dichlordiethoxyquinone-dibenzoyldiethylacetal is heated with sulphuric acid of specific gravity 1.44 it is converted into a new substance, the analysis* of which gave numbers corresponding to the formula $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2O$. This body must be formed by the saponification of two ethoxy groups by the sulphuric acid, whereas we should have expected that the acid would have attacked rather the two benzoate groups. Our experiments have not as yet given us any means of determining which pair of ethoxy groups has been saponified. From the formula established by analysis we should infer that, after the two ethoxy groups had been converted by saponification into two hydroxyls, a molecule of water was eliminated, leaving the atom of oxygen spanning the benzol ring between two atoms of carbon in the para position to each other. Our substance, therefore, would have some analogy to cineol, if the constitution ascribed to it by Brühl † is correct. We realize fully, however, that such an unusual constitution as this should not be considered estab-lished without the most convincing proof, and, as at present we are unable to give this, we propose it only as that which accords best with the results of analysis and the method of preparation of the sub-stance. We have made some attempts to prepare derivatives of this substance in order to throw light on its constitution, and have found

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* As our first analytical results approached the numbers calculated for the di-chlordiethoxyhydroquinone dibenzoate $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2$, we thought that perhaps we had in hand this substance mixed with an obstinately adhering impurity, and accordingly we made it from the substituted hydroquinone in order to compare it with our substance, but found that the two were not iden-tical, since it melts at 215°, while the melting point of our new substance is 142°. The bad results from our first analyses we found afterward to be due to the difficulty in securing a complete combustion of our saponification product, and, after taking special precautions to insure this, numbers were obtained from very carefully purified preparations agreeing excellently with those for the formula given above.

† Ber. d. ch. G., XXI. 461. Compare also Ibid., XXVII. 810.

that hydriodic acid converts it into a substance probably having the formula $C_6Cl_2OC_2H_5OH(OCOC_6H_5)_2$ and melting at 164°, but we have not yet studied this substance thoroughly enough to advance any theory in regard to its constitution. Aniline also forms one or more compounds with the saponification product, which we have not yet succeeded in bringing it into a state fit for analysis. We must content ourselves, therefore, at present with this preliminary statement of our experiments on this subject, the study of which will be continued in this laboratory during the next academic year.

The methyl compounds $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2$, melting at 193°, and $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$, melting at 205°–206°, which agree with the corresponding ethyl compounds in every respect, have also been prepared. In order to determine whether other acid radicals would act like benzoyl we treated the sodium salt of the diethyl hemiacetal with chlorocarbonic ester, and obtained the dichlordiethoxyquinone diethylacetaldicarbonic ester

$$C_6Cl_2(OC_2H_5)(OC_2H_5)_2(OCOOC_2H_5)_2,$$
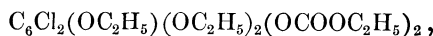
which melts at 122°–123°. In view of our experiments with the benzoyl derivative, the saponification of this substance promises interesting results.

We have tried a number of experiments to determine the limits of the formation of hemiacetals from quinones; and have found that the dibromdiphenoxyquinone, melting point 266°–267°, made from bromanil, forms a hemiacetal, which seems to be as stable as the one made from chloranil. The chlordiphenoxyquinone, melting point 169°–170°, made from trichlorquinone, also forms a hemiacetal, but this is much less stable than that containing two atoms of chlorine. Even the dimethoxydiphenoxyquinone yielded a hemiacetal, but it was so unstable that it decomposed spontaneously almost as soon as it was formed. So that the stability of the hemiacetals seems to depend on the number and strength of the negative radicals attached to the benzol ring. It was not very probable, therefore, that a hemiacetal of quinone itself could be isolated, but yet we felt it was necessary to try the experiment; and this has established the fact that quinone is acted on by sodic ethylate, although the product — a green salt — has so far resisted our attempts to purify it for analysis. Work with it is especially hard because of its very slight stability; it takes fire spontaneously, if dried in the air at ordinary temperatures; and although, if dried first in hydrogen, it does not take fire on mere exposure to the air, it glows like tinder when heated to temperatures as

low as 40°. After we had abandoned for the present the attempt to analyze the green salt, we succeeded in throwing some light on its composition by determining the proportion of quinone to sodic ethylate necessary to form it, as we found that each molecule of quinone takes up one molecule of sodic ethylate, but it must be left to future experiments to decide whether the product is really a hemiacetal.

In all the work so far described in this paper only two of the atoms of chlorine in chloranil have been replaced by other radicals; we found, however, that the other pair of atoms of chlorine could be replaced by phenoxy groups, if the dichlordiphenoxyquinone was treated with sodic phenylate, or if chloranil was acted on by four equivalents of sodic phenylate. The tetraphenoxyquinone thus formed melted at 229°–230°, and offered a rather striking resistance to the action of reducing agents, although zinc dust and glacial acetic acid converted it into tetraphenoxyhydroquinone, $C_6(OC_6H_5)_4OH$, melting point 219°–220°. Toward acids the tetraphenoxyquinone shows a marked stability, but by boiling with a strong solution of sodic hydrate it was converted into the diphenoxanilic acid, $C_6(OC_6H_5)_2(OH)_2O_2$, which melts at about 276°. Sodic methylate converts tetraphenoxyquinone into the dimethoxydiphenoxyquinone by replacing two of its phenoxy by methoxy groups; the substance melts at 171°. The corresponding diethoxydiphenoxyquinone, melting at 128°, was formed, instead of tetraphenoxyquinone, when chloranil was treated with sodic phenylate made from phenol and sodic ethylate in alcoholic solution. It is a noteworthy fact that bromanil acts differently with sodic phenylate made in this way, giving the dibromdiphenoxyquinone. One other case was observed of the substitution of all four of the chlorine atoms of chloranil. This was when the dichlorquinone dimalonic ester of Stieglitz was boiled with alcohol and sodic carbonate, as it was converted into diethoxyquinone dimalonic ester melting at 115°. It is certainly strange that such a rather weak reagent should remove these two atoms of chlorine, which in other cases have seemed very firmly attached to the molecule. In all the reactions just described it is to be observed that the chlorine atoms or phenoxy groups are replaced in pairs, and this fact also appears in much of the work with chloranil previous to ours. This replacement of the radicals two at a time can probably be connected with the para position of the two atoms of oxygen, which in this case serve to diminish the attraction of these radicals to the benzol ring, and thus make it possible to replace them, as in the case of tribromdinitrobenzol ($BrNO_2BrNO_2Br$), melting point 192°, where the loosening nitro groups are in the meta position, all three of the bromine atoms are replaced in many reactions.

EXPERIMENTAL PART.

Action of Potassic Phenylate on Chloranil.

In order to study this action, 25 grams of chloranil suspended in 50 c. c. of water were treated with an aqueous solution of potassic phenylate, made from 12 grams of potassic hydrate and 25 grams of phenol, which gave the proportion of two molecules of potassic phenylate to one of chloranil. To obtain a good result in this process it was necessary that the chloranil should not be in too large crystals; if, therefore, the specimen used was well crystallized, it was reduced to the hydroquinone with sulphurous acid, and then oxidized with nitric acid, which left it in a finely divided form easily attacked by the solution of potassic phenylate. The potassic phenylate was added in small portions at a time, and the first few drops imparted to the liquid a chrome-green color, which gradually changed to blue-black as more of the solution was added, until at last the whole became very dark blue or nearly black. In order to complete the reaction the mixture was heated on the steam bath for thirty minutes, which changed the color from black to red. In the cold there were no signs of the formation of this red substance, but it began to appear as soon as the mixture was warmed. The solution was filtered, and the dark red solid remaining on the filter, after washing thoroughly with water and alcohol, was purified by crystallization from hot benzol until it showed the constant melting point of 243°.

The analysis of the substance dried at 100° gave the following results : —

I. 0.2138 gram of the substance gave on combustion 0.4692 gram of carbonic dioxide and 0.0637 gram of water.

II. 0.1510 gram of the substance gave, according to the method of Carius, 0.1206 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_6H_5)_2O_2$.	Found. I.	II.
Carbon	59.82	59.85	
Hydrogen	2.77	3.32	
Chlorine	19.67		19.75

From these results it is evident that the substance is dichlordiphenoxyquinone. The yield is very good, 25 grams of chloranil giving as a rule 26 to 30 grams of the new substance, that is, about 80 per cent of the theoretical yield.

Properties of Dichlordiphenoxyquinone, $C_6Cl_2(C_6H_5O)_2O_2$. — The substance crystallizes from benzol in beautiful red needles arranged in rosettes. It melts at 243°, and is very slightly soluble in alcohol even when hot, less so when cold, insoluble in cold and boiling water, difficultly soluble in boiling benzol, and only very slightly soluble in the cold ; it is sparingly soluble in cold chloroform, more easily in hot, slightly soluble in cold glacial acetic acid, but easily when the acid is boiling; in ether, ligroine, carbonic disulphide, or acetone, it is insoluble. The three strong acids have no visible effect on it, hot or cold. It is readily saponified by a solution of sodic hydrate, forming chloranilic acid. It is not affected by sulphurous acid at 100° under the ordinary pressure, but is easily reduced to the corresponding hydroquinone by warming with hydriodic acid, or by the action of glacial acetic acid and zinc dust.

Dichlordiphenoxyhydroquinone, $C_6Cl_2(C_6H_5O)_2(OH)_2$.

This substance was prepared by mixing dichlordiphenoxyquinone with hydriodic acid (boiling between 123° and 126°), and heating for some time on the steam bath. The product formed by this reduction was purified by crystallization from boiling dilute alcohol (50 per cent) until it showed the constant melting point of 197°. The analysis of the substance dried at 100° gave the following results : —

I. 0.2147 gram of the substance gave on combustion 0.4678 gram of carbonic dioxide and 0.0723 gram of water.

II. 0.1578 gram of the substance gave by the method of Carius 0.1244 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_6H_5)_2(OH)_2$.	Found. I.	II.
Carbon	59.51	59.41	
Hydrogen	3.31	3.73	
Chlorine	19.56		19.49

The change from the quinone to the hydroquinone is quantitative.

Properties of Dichlordiphenoxyhydroquinone. — It crystallizes from dilute alcohol (50 per cent) in large colorless prisms, or in little needles very much branched, forming thick arborescent masses which melt at 197°–198°, and are readily soluble in ethyl alcohol, methyl alcohol, or acetone ; soluble in carbonic disulphide or hot glacial acetic acid ; slightly soluble in chloroform, cold glacial acetic acid, or ether. It is insoluble in water, either cold or hot, benzol, or ligroine. Dilute or strong sulphuric acid or hydrochloric acid does not act on the di-

chlordiphenoxydroquinone even when hot.   It dissolves in alkalies and
is reprecipitated from the solution by acids.   On long standing or
boiling with sodic hydrate it is saponified, giving the sodium salt of
chloranilic acid which separates in long dark carmine red needles.

By the action of oxidizing agents, such as ferric chloride, dilute
nitric acid, or potassic dichromate in acid solution, it is easily changed
to the corresponding quinone.

Action of Aniline on Dichlordiphenoxyquinone.

The dichlordiphenoxyquinone was treated with aniline in the expec-
tation of removing the two remaining atoms of chlorine.   For this
purpose 1 gram of dichlordiphenoxyquinone was mixed with 5 grams
of aniline, and the mixture warmed on the water bath for a few min-
utes.   When cool, the large excess of aniline was removed by dilute
sulphuric acid, and, after thorough washing, the dark-colored residue
was purified by dissolving it in aniline, and then adding a small quan-
tity of alcohol; in this way well formed dark brown crystals were
obtained, melting at $287°-290°$, and therefore probably the dichlor-
dianilidoquinone, the melting point of which is given as $285°-290°$.
This substance was first prepared and studied by O. Hesse,[*] later by
Knapp and Schultz.[†]   To confirm this inference the crystals were dried
at $100°$ and the chlorine determined.

0.1480 gram of the substance gave by the method of Carius 0.1174
gram of argentic chloride.

	Calculated for $C_6Cl_2(C_6H_5NH)_2O_2$	Found.
Chlorine	19.70	19.61

The reaction therefore took an unexpected course, since the anilido
groups replaced the two phenoxy radicals instead of the two atoms of
chlorine.

Action of Sodium Malonic Ester on Dichlordiphenoxyquinone.

It has been shown in the preceding section that aniline removes the
phenoxy groups instead of the atoms of chlorine from dichlordiphenoxy-
quinone.   We therefore next turned our attention to the action of
sodium malonic ester upon it to see whether this reagent behaved in
the same way.   In order to study this reaction 1 gram of dichlordi-
phenoxyquinone suspended in 10 c.c. of absolute alcohol was treated

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[*] Ann. Chem., CXIV. 306.   [†] Ibid., CCX. 187.

with a little more than two equivalents of sodium malonic ester, which
was made by treating 0.15 gram of metallic sodium with about 10 c.c.
of absolute alcohol, and then adding 2 grams of malonic ester.   On
adding the sodium malonic ester, the solution turned very dark blue,
and on standing a dark blue precipitate separated, which was filtered
off and washed with alcohol, in which it is only slightly soluble.   The
precipitate dissolved readily in water with a beautiful blue color, and
on the addition of an acid a slightly yellow crystalline product sepa-
rated, which was purified by recrystallization from boiling dilute
alcohol until it gave the constant melting point 132°.   After drying
at 100°, it gave the following results on analysis : —

I. 0.2180 gram of the substance gave on combustion 0.3880 gram of
carbonic dioxide and 0.0994 gram of water.

II. 0.1654 gram of the substance gave 0.0964 gram of argentic
chloride.

	Calculated for $C_6Cl_2[CH(COOC_2H_5)_2]_2O_2.$	Found. I	II.
Carbon	48.68	48.53	
Hydrogen	4.46	5.06	
Chlorine	14.41		14.41

These results prove that the substance is dichlorquinonedimalonic
ester.   Four grams of the dichlordiphenoxyquinone gave a yield of
about 1.5 grams of the malonic ester compound, that is, 27 per cent of
the theoretical yield.

It is evident that this body must be formed through the replace-
ment of the two phenoxy groups by two malonic ester radicals, and
in fact it was not hard to detect the phenol, which formed the second-
ary product of the reaction.   For this purpose the alcoholic filtrate
from the sodium salt of the malonic ester derivative, after evaporation
nearly to dryness, was diluted with water, and treated with a dilute
acid, when the smell of phenol was very evident, and bromine water
gave a voluminous white precipitate.   This easy replacement of the
phenoxy groups by the malonic ester radicals, even although the for-
mer are attached to a benzol ring, suggests other work in the same
line, which will be undertaken in this Laboratory.

This dichlorquinonedimalonic ester crystallizes from dilute alcohol
in long slender radiating needles of a yellow color, which melt at
132°, and are insoluble in cold or boiling water, soluble in cold or
warm alcohol.   It is not affected by weak oxidizing agents, but hydri-
odic acid reduces it to a white crystalline substance, which melts at

159°–160°, the melting point of the dichlorhydroquinonedimalonic ester discovered by J. Stieglitz ; * our dichlorquinonedimalonic ester is therefore identical with that obtained by him from the direct action of sodium malonic ester on chloranil. Our indirect method of preparing it, however, gives a better yield than the direct method, 27 per cent instead of 10 per cent. That we might not intrude on this field of research already occupied by Stieglitz, we have confined our work on this substance to that necessary for establishing its identity.

Sodium Salt of Dichlorquinonedimalonic Ester,
$$C_6Cl_2(CNa(COOC_2H_5)_2)_2O_2.$$

In order to prepare this salt the dichlorquinonedimalonic ester was dissolved in ether, and treated with rather less than the required amount of sodic ethylate in a strong alcoholic solution. The sodium salt separated at once as a blue precipitate, which was repeatedly washed with ether by decantation, and dried over sulphuric acid and paraffine until the weight remained constant, after which the sodium was determined with the following result : —

0.2788 gram of the salt gave 0.0731 gram of sodic sulphate.

	Calculated for $C_6Cl_2(CNa(COOC_2H_5)_2)_2O_2.$	Found.
Sodium	8.57	8.49

The sodium salt has a beautiful blue color, and is very easily soluble in water, giving a solution of a blue color as intense and striking as that of aniline blue. It is somewhat soluble in alcohol, but insoluble in ether.

Diethoxyquinonedimalonic Ester, $C_6(OC_2H_5)_2(CH(COOC_2H_5)_2)_2O_2.$

In the first attempt to form the sodium salt of the dichlorquinone-dimalonic ester, the substance was dissolved in absolute alcohol and boiled with an excess of dry sodic carbonate. When the sodic carbonate was first added, the alcoholic solution was colored dark blue ; but after filtering out the excess of sodic carbonate and evaporating rapidly, the solution became nearly colorless, and left after the alcohol had been driven off a residue of almost white crystals, which were purified by crystallization from alcohol until the melting point remained constant at 115°. The analysis of the substance dried over sulphuric acid and paraffine gave the following results : —

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* Am. Chem. Journ., XIII. 38.

0.2010 gram of the substance gave on combustion 0.4122 gram of
carbonic dioxide and 0.1242 gram of water.

	Calculated for $C_6(OC_2H_5)_2[CH(COOC_2H_5)_2]_2O_2$	Found.
Carbon	56.25	55.93
Hydrogen	6.25	6.86

It gave no test for chlorine. These results prove that the substance
is diethoxyquinonedimalonic ester, and it is certainly strange that this
substance should have been formed from the corresponding dichlor
compound by the action of sodic carbonate and alcohol, in view of
the fact that these two atoms of chlorine in other cases have proved
hard to replace. The substance crystallizes in beautiful yellowish
white needles melting at 115°, which are insoluble in water, readily
soluble in alcohol or ether.

*Action of Sodic Methylate on Dichlordiphenoxyquinone.—Dichlordime-
thoxyquinone Dimethylhemiacetal*, $C_6Cl_2(OCH_3)_2(OH)_2(OCH_3)_2$.

In order to see whether the phenoxy groups in dichlordiphenoxy-
quinone would be removed by sodic methylate, as they were when it
was treated with sodium malonic ester or aniline, 10 grams of the
dichlordiphenoxyquinone were mixed with a methyl alcohol solution
of a little less than four equivalents of sodic methylate, made by treat-
ing 2.5 grams of metallic sodium with 60 c.c. of methyl alcohol. The
solution was warmed gently on the water bath, and stirred constantly ;
soon a white crystalline substance began to separate, and the red color
of the dichlordiphenoxyquinone disappeared entirely. The solution
was filtered, the residue washed with a little alcohol, dissolved in
water, filtered again, and then treated with dilute sulphuric acid in
excess, which set free a white insoluble compound. The proper-
ties of this substance indicated at once that the reaction had not con-
sisted in a simple replacement of the phenoxy by methoxy groups,
as in that case the product must have been the dichlordimethoxy-
quinone discovered by Kehrmann,* which is red, melts at 141°–142°,
and is not insoluble in the common solvents. To prepare our new
body for analysis it was filtered off, washed with water, alcohol, and
then with water again; after which it was dissolved in dilute sodic
hydrate, filtered, precipitated with dilute sulphuric acid, and washed
thoroughly as described above. This treatment was repeated two or
three times, until the substance was perfectly white and did not change

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* Journ. Prakt. Chem., [2.], XL. 370.

color when washed with alcohol and ether, and then dried for a short time over sulphuric acid and paraffine. It was then analyzed with the following results : —

    I. 0.2410 gram of the substance gave on combustion 0.3459 gram of carbonic dioxide and 0.1064 gram of water.

    II. 0.2005 gram of the substance gave on combustion 0.2943 gram of carbonic dioxide and 0.9720 gram of water.

    III. 0.1920 gram of the substance gave by the method of Carius 0.1851 gram of argentic chloride.

    IV. 0.2372 gram of the substance gave by the method of Carius 0.2233 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	I.	II.	III.	IV.
			Found.		
Carbon	39.87	39.13	40.02		
Hydrogen	4.65	4.90			
Chlorine	23.59			23.83	23.28

These results indicate that the substance is a dimethoxydichlor-quinone, to which two molecules of methyl alcohol have been added. To confirm this view of its composition the sodium salt was prepared and analyzed as follows. An excess of the insoluble compound was added to a solution of sodic methylate in a large quantity of methyl alcohol. As the sodium salt formed is soluble in methyl alcohol,* while the original compound is not, it was easy by filtering to obtain a pure solution of the salt, from which it was then precipitated by adding an excess of ether. The precipitate was repeatedly washed with ether by decantation, transferred to a weighed platinum crucible, dried over sulphuric acid and paraffine, and analyzed with the following results : —

    I. 0.2372 gram of the salt gave 0.0828 gram of sodic sulphate.

    II. 0.2887 gram of the salt gave 0.1025 gram of sodic sulphate.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	I.	II.
		Found.	
Sodium	11.24	11.31	11.50

As these analyses indicate that the salt contains two molecules of methyl alcohol of crystallization, an attempt was next made to determine the amount of volatile matter which it contained, with the following result : —

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* In the preparation of the original substance the sodium salt was obtained as a precipitate, because the amount of methyl alcohol used was not enough to dissolve it.

0.3177 gram of the salt heated at 100° lost 0.0501 gram.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2(CH_3OH)_2$.	Found.
Methyl Alcohol	15.64	15.77

Another sample of the sodium salt was then dried at 100° to a constant weight, and a sodium determination was made in the dry substance.

0.2422 gram of the salt gave 0.1018 gram of sodic sulphate.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3ONa)_2$.	Found.
Sodium	13.33	13.61

These results show that, by the action of sodic methylate upon the dichlordiphenoxyquinone in the first place the two phenoxy groups are replaced by two methoxy groups, and then two molecules of sodic methylate are added directly to the molecule of dichlordimethoxy-quinone formed by the first part of the action. The proof that these two molecules of sodic methylate are attached to the carbonyl groups of the quinone has been given in the introduction to this paper, and the new substance therefore is dichlordimethoxyquinone dimethyl-hemiacetal.

Other Methods of Preparing the Dichlordimethoxyquinone Dimethylhemiacetal.

This body can be made also directly from chloranil by the action of sodic methylate. When one equivalent of chloranil was treated with five or six equivalents of sodic methylate dissolved in methyl alcohol, a green salt containing sodium separated. This salt was dissolved in water rendered alkaline by a little sodic hydrate, and the addition of a dilute acid to this solution produced a dirty white precipitate, a portion of which was soluble in alcohol, while the rest remained undissolved. The insoluble part, after purification by dissolving in sodic hydrate and filtering, was precipitated again with dilute sulphuric acid, and washed with water and alcohol, after which it was dried in a desiccator, and the chlorine determined : —

0.2060 gram of the substance gave by the method of Carius 0.1962 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2O_2(CH_3OH)_2$.	Found.
Chlorine	23.59	23.55

That this product was the same as that prepared from the dichlor-diphenoxyquinone was shown also by its properties, which agreed with those observed for that substance, especially by its very characteristic reaction with dilute acids.

The other product obtained from the green salt formed by the action of sodic methylate on chloranil was dissolved in the alcohol used in washing the dirty white precipitate from dilute sulphuric acid; after evaporating off the alcohol, it was purified by recrystallization from dilute alcohol, and analyzed with the following result: —

> 0.2094 gram of the substance gave by the method of Carius 0.4841
> gram of argentic chloride.

	Calculated for $C_6Cl_4(OH)_2$.	Found.
Chlorine	57.25	57.16

As it melts at 235°, there can be no doubt that it is the tetrachlorhydroquinone, the melting point of which is given by Sutkowski [*] as 232°. We are unable to determine at present whether this tetrachlorhydroquinone is due to a secondary reaction, or whether it proceeds from that by which the hemiacetal is made. Sodic ethylate does not act in this way with chloranil.

The dichlordimethoxyquinone dimethylhemiacetal is also formed when dichlordimethoxyquinone melting at 141°–142° is treated with two equivalents of sodic methylate dissolved in methyl alcohol.

Properties of the Dichlordimethoxyquinone Dimethylhemiacetal. — It is a white amorphous solid, insoluble in all the common solvents. It is very easily converted into the red dichlordimethoxyquinone, melting at 141°–142°, discovered by Kehrmann.[†] This change can be effected by heat alone, since in the neighborhood of 160° it begins to take on a slight reddish color, which becomes darker very slowly at this temperature, but when heated to 195° or higher the substance melts to a red liquid, at the same time increasing very much in volume and giving off many bubbles of gas consisting probably of the vapor of methyl alcohol. The decompostion point is not a definite one, as in different trials this action took place at temperatures sometimes as much as twenty or twenty-five degrees apart. An easier way to bring about this change is by treating the hemiacetal with dilute sulphuric acid or dilute hydrochloric acid, to either of which it shows itself remarkably susceptible, the decomposition taking place quanti-

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[*] Ber. d. ch. G., XIX. 2316.   [†] Journ. Prakt. Chem., [2.], XL. 370.

tatively, slowly in the cold, but quickly on warming. The ease with which it is attacked by dilute acids is its most striking property. Continued boiling with water or with dilute alcohol or glacial acetic acid brings about the same decomposition, as does also treatment of either the free substance or its sodium salt with benzoylchloride in a sealed tube at 100°, methyl benzoate being the secondary product. Acetic anhydride decomposes it in the same way, but more slowly; on the other hand, neither methyl nor ethyl iodide acts on the sodium salt or the free substance. The formation of the benzoic ester of the substance is described below.

The hemiacetal is a weak acid, forming with sodic methylate the white crystalline sodium salt, the method of preparation and analyses of which have been given above. This salt is soluble in water or alcohol, insoluble in ether. With argentic nitrate a white non-crystalline silver salt is formed, which is insoluble in water, and easily decomposed.

Action of Sodic Ethylate on Dichlordiphenoxyquinone. — Dichlordiethoxyquinone Diethylhemiacetal, $C_6Cl_2(OC_2H_5)_2(OH)_2(OC_2H_5)_2$.

In order to study this action 10 grams of dichlordiphenoxyquinone were treated with an alcoholic solution of little less than four equivalents of sodic ethylate, which was made by treating 2.5 grams of metallic sodium with 60 c.c. of absolute alcohol. When the sodic ethylate was first added there was no apparent action, but on standing, even in the cold, the red color of the dichlordiphenoxyquinone gradually disappeared, and a white crystalline sodium salt was formed. After warming gently on the water bath to finish the reaction, the solution was filtered, the salt washed with alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and then with water again. In order to purify the substance further, it was dissolved in dilute sodic hydrate, filtered, precipitated again with dilute sulphuric acid, and washed thoroughly, as above. This treatment was repeated until finally the substance was perfectly white, and did not change color when washed with alcohol and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results : —

I. 0.2205 gram of the substance gave on combustion 0.3802 gram of carbonic dioxide and 0.1304 gram of water.

II. 0.2017 gram of the substance gave by the method of Carius 0.1614 gram of argentic chloride.

	Calculated for	Found.	
	$C_6 Cl_2 (OC_2H_5)_2O_2(C_2H_5OH)_2.$	I.	II.
Carbon	47.06	47.02	
Hydrogen	6.16	6.57	
Chlorine	19.89		19.78

These results show that the action of the sodic ethylate on the dichlordiphenoxyquinone is analogous to that of sodic methylate, since two phenoxy groups are replaced by two ethoxy groups, and then two molecules of sodic ethylate are added directly to one molecule of the dichlordiethoxyquinone thus formed, giving the sodium salt of dichlordiethoxyquinone diethylhemiacetal. The yield of the sodium salt from 10 grams of dichlordiphenoxyquinone was usually a little less than 10 grams, and therefore, as the change from the sodium salt to the hemiacetal is nearly quantitative, we obtained over 75 per cent of the theoretical yield.

Properties of the Dichlordiethoxyquinone Diethylhemiacetal. — It is a white amorphous solid, which dissolves slightly in alcohol, but is partially decomposed by this solvent, so that it cannot be recrystallized from it. It is essentially insoluble in all the other common solvents. By boiling with dilute sulphuric or hydrochloric acid it is decomposed, and the same reaction takes place more slowly when it stands with the dilute acid in the cold. The product of the action in either case is a light red body melting at 104°–105°, after being purified by crystallization from alcohol, which is, therefore, dichlordiethoxyquinone, as this is the melting point ascribed to this substance by Kehrmann.* Stenhouse,† who discovered it, gives its melting point as 107°; but even by repeated recrystallization we have not been able to raise the melting point above 104°–105°, and therefore have come to the conclusion that Stenhouse's higher number must be due to an error. The white insoluble hemiacetal melts at 140°–143°, or rather decomposes at this temperature, changing into the red dichlordiethoxyquinone, which then melts. From these properties it appears that the relationship between the diethyl and dimethylhemiacetals is of the closest sort.

Like the corresponding methyl compound the dichlordiethoxyquinone diethylhemiacetal has acid properties forming with sodic hydrate a sodium salt. It shows toward sodic hydrate a stability in marked contrast to its susceptibility to the action of dilute acids, as it is neces-

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* Journ. Prakt. Chem., [2.], XL. 365.   † Ann. Chem., Suppl. VIII. 14.

sary to boil it with a strong solution of sodic hydrate in order to
saponify it to chloranilic acid.   The sodium salt of the diethylhemia-
cetal is white and crystalline, readily soluble in water, slightly soluble
in alcohol, and insoluble in ether.   The dried salt is slowly decom-
posed on standing in a closed bottle for several weeks, alcohol is given
off, and a solid product left, which contains some sodic chloranilate
and another body, or more than one, which we have not yet identified.
The silver salt is insoluble, and has a slight brownish yellow color.
It is blackened by light alcohol being set free.   On warming with
water a red substance is formed, probably chloranilic acid.   Insoluble
salts were also obtained with solutions containing barium, calcium,
lead, or zinc, but they were not studied.   The details of the prepara-
tion of the sodium and silver salts will be found under the preparation
of dichlordiethoxyquinone tetraethylacetal later in this paper.

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Dichlordimethoxyquinone   Diethylhemiacetal,
$C_6Cl_2(OCH_3)_2(OH)_2(OC_2H_5)_2.$

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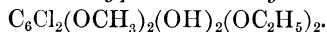
This substance was made by treating 0.9 gram of dichlordimethoxy-
quinone with an alcoholic solution of sodic ethylate made from 0.2
gram of metallic sodium and absolute alcohol.   After warming the
mixture for a few minutes, all the red dichlordimethoxyquinone disap-
peared, and a crystalline sodium salt was deposited.   The liquid was
then cooled, the precipitate filtered out, washed with a little alcohol, and
dissolved in water, in which it is completely and easily soluble.   The
aqueous liquid after filtration was treated with dilute sulphuric acid,
which threw down a white bulky precipitate of the free hemiacetal,
and this, after thorough washing with water, alcohol, and ether, was
dried over sulphuric acid and paraffine, and analyzed with the follow-
ing result : —

0.1892 gram of the substance gave by the method of Carius 0.1627
    gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OH)_2(OC_2H_5)_2.$	Found.
Chlorine	21.58	21.26

The dichlordimethoxyquinone diethylhemiacetal, like those hemia-
cetals which have been described already, is an amorphous white solid,
essentially insoluble in all the common solvents.   It is decomposed at
temperatures between 140° and 160°, forming a red substance, prob-
ably dichlordimethoxyquinone, and it is easily saponified by dilute
acids.

Dichlordiethoxyquinone Tetraethylacetal, $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$.

It has been stated already that ethyl or methyliodide did not act either on the free hemiacetal or its sodium salt; if, however, the silver salt of dichlordiethoxyquinone diethylhemiacetal was treated with ethyliodide, the corresponding tetraethylacetal was formed. As this compound could be obtained only in very small quantities and with great difficulty, it was necessary to prepare the sodium and silver salts of the hemiacetal on a large scale, which was done as follows. 40 grams of dichlordiphenoxyquinone were mixed with the sodic ethylate made by treating 10 grams of metallic sodium with 150 c.c. of absolute alcohol, and in order to complete the reaction the mixture was warmed on the steam bath for a few minutes, and then allowed to stand at ordinary temperatures for four or five hours. The sodium salt of the dichlordiethoxyquinone diethylhemiacetal, which separated in large amount, was filtered off, and washed thoroughly, first with a mixture consisting of equal parts of alcohol and ether, and finally with ether alone. In this way 40 to 42 grams of the essentially pure sodium salt were obtained instead of the 44 grams required by the theory; the yield, therefore, was between 90 and 95 per cent of the theoretical.

In order to prepare the silver salt of the diethylhemiacetal, a concentrated aqueous solution of the sodium salt was treated with 25 grams of argentic nitrate dissolved in a small amount of water. The insoluble silver salt was filtered, washed thoroughly with water, alcohol, and ether, and then dried as quickly as possible by sucking a stream of air through it on the filter pump.

The silver salt of the dichlordiethoxyquinone diethylhemiacetal was then suspended in ether, and treated in the cold with ethyl iodide, when, in addition to a very small quantity of the tetraethylacetal, a large amount of dichlordiethoxyquinone was obtained. The acetal was separated from the quinone by treating the products of the reaction with a dilute solution of sodic hydrate in 50 per cent alcohol, which converted the dichlordiethoxyquinone into the sodium salt of chloranilic acid, while the dichlordiethoxyquinone tetraethylacetal was not affected by it. By washing with water it was then easy to separate the freely soluble sodic chloranilate from the insoluble acetal, which was purified by recrystallization from ligroine until it showed the constant melting point 101°–102°, when it was dried in a desiccator, and on analysis gave the following results : —

   I. 0.2039 gram of the substance gave on combustion 0.3928 gram of carbonic dioxide and 0.1335 gram of water.

II. 0.2177 gram of the substance gave on combustion 0.4181 gram
     of carbonic dioxide. The water determination was lost.
III. 0.1843 gram of the substance gave by the method of Carius
     0.1304 gram of argentic chloride.
IV. 0.1620 gram of the substance gave 0.1135 gram of argentic
     chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5)_4$.	I.	Found. II	III.	IV.
Carbon	52.30	52.54	52.37		
Hydrogen	7.26	7.28	—		
Chlorine	17.19			17.49	17.32

The yield, as has been already stated, is very small.

Properties of Dichlordiethoxyquinone Tetraethylacetal. — This sub-
stance can be obtained from ligroine in good-sized white rhombic
prisms, but when more rapidly crystallized it forms irregularly fan-
shaped groups of very much branched needles resembling certain
delicate seaweeds, or four-sided plates nearly but not quite rectangu-
lar and much striated. It melts at 101°–102°. By heating in a
capillary tube it is apparently not decomposed even at so high a tem-
perature as 275°, but between 260° and 275° it sublimes, giving
beautiful white crystals in the upper part of the tube. It is very
easily soluble in ether, benzol, alcohol, chloroform, acetone, ligroine,
glacial acetic acid, carbonic disulphide, acetic anhydride, or methyl
alcohol, but is insoluble in water. Ligroine is the best solvent for it.

It is saponified by sulphuric acid of specific gravity 1.44, giving
the dichlordiethoxyquinone melting at 104°–105°, and also a small
quantity of chloranilic acid. In the cold the acid produces little or
no effect on the acetal, but after warming on the steam bath for half
an hour the saponification is complete. A more dilute acid seems to
have no action upon it. Sodic hydrate, even when boiling or mixed
with alcohol, does not decompose the acetal.

The differences between the properties of the tetraethylacetal and
the diethylhemiacetal certainly are remarkable. The hemiacetal is
entirely insoluble, while the acetal is exceedingly soluble in all the
common solvents except water. The former is very unstable, being
readily decomposed by even very dilute acids, while the latter is sa-
ponified only slowly by comparatively strong acids when heated with
them. By heat also the hemiacetal is easily decomposed, whereas
the acetal sublimes apparently unaltered at high temperatures.

The action of bromine on the tetraethylacetal might prove of great
interest, as the formation of addition products from it similar to those

obtained by J. U. Nef * from quinone would prove that the four
ethoxy groups were attached to the carbonyl radicals of the quinone
molecule, and thus settle the constitution of this whole class of com-
pounds. The chances of the formation of such addition compounds
were, however, small, as Nef has shown † that dichlordiethoxyquinone
does not take up bromine, a result which we can confirm; neverthe-
less we felt that it would be unwise to neglect this experiment.
Accordingly, 0.5 gram of bromine dissolved in chloroform was added
to 0.5 gram of the acetal also dissolved in dry chloroform. Even the
first drop of the bromine imparted a distinct yellowish red color to
the solution, showing that no bromine addition compound had been
formed. When all the bromine had been added, the solution was
allowed to evaporate spontaneously, and, although the residue was
colored slightly, it was found that the weight had not increased, and
after one recrystallization from ligroine it gave the melting point of
the unaltered acetal 101°–102°. In another experiment the chloro-
form solution was evaporated to dryness on the water bath, and the
same results were obtained. Under no conditions that we have found
could the acetal be induced to take up bromine. The negative out-
come of these experiments cannot be used in deciding the constitution
of the acetal, since its inability to take up bromine is more likely to
be due to the presence of the two atoms of chlorine and two ethoxy
groups attached to the benzol ring than to the occupation of the
double bonds by the four additional ethoxy groups, since dichlordie-
thoxyquinone does not take up bromine, as has been already stated.

Dichlordiethoxyquinone Dibenzoyldiethylacetal,
$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2.$$

When the diethylhemiacetal itself or its sodium salt was treated
with benzoyl chloride at 100° in a sealed tube, no benzoyl compound
was formed, but the main products were dichlordiethoxyquinone and
ethylbenzoate. A similar result was obtained when the sodium or
silver salt of the hemiacetal was suspended in ether, and then treated
with benzoyl chloride. When, however, the sodium salt was sus-
pended in alcohol instead of ether and benzoyl chloride added, the
dibenzoyl derivative was readily formed, and only a trace of dichlordie-
thoxyquinone was produced. The following method was found to be
the best for the preparation of this substance. To 10 grams of the
sodium salt of the dichlordiethoxyquinone diethylhemiacetal suspended

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* Amer. Chem. Journ., XII. 483.   † Ibid., XI. 20.

in a small quantity of alcohol 7.6 grams of benzoyl chloride were added, which gave the proportion of two molecules of benzoyl chloride to one of the sodium salt.   There was but little action in the cold, but when the mixture was warmed on the water bath the reaction took place readily, with the separation of sodic chloride.   After cooling, the solution was filtered, and the solid remaining on the filter washed thoroughly with alcohol and water, and then crystallized from hot alcohol until it showed the constant melting point 170°.   The analysis of the substance dried at 100° gave the following results : —

I.   0.2428 gram of the substance gave on combustion 0.5276 gram of carbonic dioxide and 0.1230 gram of water.
II.   0.2173 gram of the substance gave by the method of Carius 0.1112 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OC_2H_5OCOC_6H_5)_2$.	Found. I.	II.
Carbon	59.47	59.27	
Hydrogen	5.31	5.63	
Chlorine	12.57		12.65

The yield of the dichlordiethoxyquinone-dibenzoyldiethylacetal from ten grams of the salt is seven and one half grams, or about 66 per cent of the theoretical yield.

Properties of Dichlordiethoxyquinone Dibenzoyldiethylacetal. — From alcohol it crystallizes in short thick prisms, or, when crystallized more rapidly, in rhombic crystals with a sharp terminal angle, often collected into curving radiated or bladed groups.   It is white, and melts at 170°.   It is easily soluble in chloroform, carbonic disulphide, ether, or benzol ; also in hot ethyl or methyl alcohol, but only slightly soluble in either of these liquids when cold ; soluble in warm glacial acetic acid ; slightly soluble in hot ligroine ; insoluble in water.   Sulphuric acid of specific gravity 1.44 saponifies it, forming the compound described in the next section.   Sodic hydrate solution, even if boiling or mixed with alcohol, does not decompose it.

The study of the action of reducing agents and of hydroxylamine on the dichlordiethoxyquinone dibenzoyldiethylacetal was of especial interest, because it threw so much light upon the constitution of this whole class of substances.   If this body was a true acetal, these agents should have no action upon it ; if, on the other hand, the ethoxy and benzoyl radicals were not attached to the two carbonyl groups of the quinone molecule, but to the four other atoms of carbon, the substance

would be converted into a secondary alcohol by reducing agents, and
into an oxime by hydroxylamine. The reducing agent selected was
a mixture of zinc dust and glacial acetic acid, as this had proved
rather the most effective for the conversion of a quinone into a hydro-
quinone, and there was little or no danger that it would saponify the
compound. Even after long continued action there were no signs of
reduction, but the unaltered dichlordiethoxyquinone dibenzoyldiethyl-
acetal was recovered from the mixture. This experiment, therefore,
goes to prove that the substance is an acetal, and this proof is strength-
ened by the fact that dichlordiethoxyquinone is converted into the
corresponding hydroquinone quickly and easily by this reducing mix-
ture.

To try the action of hydroxylamine 0.2 gram of the dichlordiethoxy-
quinone dibenzoyldiethylacetal dissolved in alcohol was mixed with
an alcoholic solution of 0.5 gram of hydroxylamine chloride. The
solution was boiled over the free flame for half an hour, and then after
cooling treated with a large excess of water. The precipitate thus
formed after one crystallization from alcohol melted at 170°, and was
therefore the unchanged original substance. No other organic sub-
stance could be found in the precipitate, or in the aqueous filtrate.
The experiment was repeated with an alkaline solution, and again
with an acid solution, but in no case could any change in the original
acetal be detected. To prove that the indifference of the acetal to the
hydroxylamine was not due to the effect of the ethoxy radicals and
chlorine atoms attached to its benzol ring, we next studied the action
of the chloride of hydroxylamine on dichlordiethoxyquinone. For
this purpose 0.5 gram of it were treated with the chloride of hydrox-
ylamine in alcoholic solution, and the mixture warmed for sixteen hours
on the water bath. Water precipitated a black substance crystallized
in scales, which was thoroughly washed with water to remove all the
hydroxylamine salt. It dissolved easily in sodic hydrate, and from
this solution acids threw down a reddish gelatinous precipitate. It
gave a good test for nitrogen by the potassium method. There can
be no doubt, therefore, that the chloride of hydroxylamine acts on
dichlordiethoxyquinone and consequently the indifference of our acetal
to this reagent is not due to the presence of the radicals attached to
the benzol ring, but is caused by the occupation of the two carbonyl
groups by the ethoxy and benzoyl radicals. As we had accomplished
our purpose when we had proved that the chloride of hydroxylamine
acts on dichlordiethoxyquinone, we have not tried to study the product
more carefully.

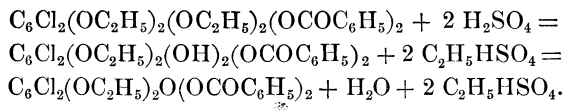*Saponification of Dichlordiethoxyquinone Dibenzoyldiethylacetal.*

This substance was boiled with sulphuric acid of specific gravity 1.44 for half an hour in a flask with a return condenser ; a certain amount of gas was given off, and the solid finally went into solution completely, but upon cooling crystals were deposited, the amount of which was increased by diluting the acid with water. This crystal-line precipitate was filtered out, washed repeatedly with water to remove a little chloranilic acid which had been formed in the process, and the residue recrystallized from alcohol until it showed the constant melting point 142°, when it was dried for analysis. The analysis of this substance gave a great deal of trouble ; by using a boat and a stream of oxygen according to the usual method we were unable to secure complete combustion, and therefore were forced to mix the compound with cupric oxide, and carry on the combustion in an old-fashioned closed tube. This accounts for the fact that our percentages of hydrogen are somewhat high.

   I.   0.2119 gram of the substance gave on combustion 0.4558 gram of carbonic dioxide and 0.0845 gram of water.

  II.   0.2062 gram gave 0.4452 gram of carbonic dioxide and 0.0869 gram of water.

III.   0.2020 gram gave 0.4344 gram of carbonic dioxide and 0.0830 gram of water.

IV.   0.2063 gram gave 0.4451 gram of carbonic dioxide and 0.0837 gram of water.

  V.   0.1947 gram of the substance gave by the method of Carius 0.1136 gram of argentic chloride.

VI.   0.2212 gram gave 0.1290 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2O$.	I.	II.	III.	Found. IV	V.	VI.
Carbon	58.65	58.66	58.88	58.64	58.84		
Hydrogen	4.07	4.43	4.67	4.56	4.51		
Chlorine	14.46					14.42	14.41

The formula calculated from these analytical results is so strange, that we were at first unwilling to accept it, and thought that perhaps we had the dibenzoate of dichlordiethoxyhydroquinone in our hands, the calculated percentages of hydrogen and chlorine for which agree fairly well with those found by us, whereas the calculated percentage of carbon is over two per cent higher. This difference we thought might be due to an obstinate impurity, and accordingly we prepared

this dibenzoate from dichlordiethoxyhydroquinone, and found that it was entirely different from the saponification product, as it melts at 215° instead of 142°. The description of this substance is given later in the paper. The supposition that the substance might contain an obstinately adhering impurity was disposed of by frequent recrystallizations. The sample for Analysis I. was crystallized only three or four times, that for II. and III. ten times, that for IV. eight times. There was no difference in the melting points of these three samples, and, as the results given above show, no essential difference in their percentage composition. We must therefore accept the formula derived from these analyses, and the most probable hypothesis is that the atom of oxygen spans the benzol ring between two atoms of carbon in the para position, but we are unable to determine at present whether this atom of oxygen proceeded from the saponification of the ethoxy radicals of the acetal, and therefore lies between the two atoms of carbon to which the benzoate groups are attached, or from the two ethoxy groups of the chloranilic ester, and therefore spans the ring between two other atoms of carbon. This latter supposition seems to us the more probable, as it would give some explanation of the ease with which the ethyls are removed. We wished to confirm such an unusual hypothesis by studying the derivatives of this substance, but our work in this direction has not yet brought any conclusive evidence in regard to its constitution, and we therefore propose this theory only as the most probable one, leaving to future work the testing of its accuracy. It may be observed here that such a substance would be a natural product of the saponification of dichlordiethoxyquinone dibenzoyldiethylacetal as shown by the following reactions : —

$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOC_6H_5)_2 + 2\ H_2SO_4 =$$
$$C_6Cl_2(OC_2H_5)_2(OH)_2(OCOC_6H_5)_2 + 2\ C_2H_5HSO_4 =$$
$$C_6Cl_2(OC_2H_5)_2O(OCOC_6H_5)_2 + H_2O + 2\ C_2H_5HSO_4.$$

We would call the substance, in accordance with its provisional formula, oxide of dichlordiethoxyhydroquinone dibenzoate, although it may be instead the oxide of dichlorquinone ethylbenzoylacetal.

Properties of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate. — It crystallizes in white well developed six-sided prisms, often of considerable size, belonging either to the hexagonal or orthorhombic system. When crystallized more quickly, it forms rather loose rosettes of prisms terminated by several planes forming a very blunt end. It shows a strong tendency to separate from its solutions in the

form of a varnish, this result being obtained, for instance, when the alcoholic solution is evaporated to dryness on the water bath. It melts at 142°, and is readily soluble in alcohol or chloroform ; soluble in carbonic disulphide, glacial acetic acid, or benzol ; difficultly soluble in ether ; insoluble in water. The best solvent for it is alcohol. With aniline it gives two or more products, the study of which next year we hope may throw some light on its constitution.

Reduction of the Oxide of Dichlordiethoxyhydroquinone Dibenzoate.

When the substance described in the preceding paragraph is moistened with a concentrated solution of hydriodic acid, and heated on the water bath until dry, a reaction takes place, as shown by the separation of free iodine. In order to complete the action the moistening with hydriodic acid and warming was repeated, and the product thus obtained was purified by repeated recrystallization from a very small quantity of alcohol until it showed the constant melting point 164°, when it was dried at 100°, and analyzed with the following results : —

I. 0.2004 gram of the substance gave on combustion 0.4339 gram of carbonic dioxide and 0.0812 gram of water.

II. 0.2301 gram of substance gave 0.5001 gram of carbonic dioxide and 0.0825 gram of water.

III. 0.2274 gram of substance gave by the method of Carius 0.1462 gram of argentic chloride.

IV. 0.1998 gram gave 0.1276 gram of argentic chloride.

V. 0.1990 gram gave 0.1276 gram of argentic chloride.

	Calculated for $C_6Cl_2OC_2H_5OH(OCOC_6H_5)_2$.	I.	II.	Found. III.	IV.	V.
Carbon	59.06	59.06	59.28			
Hydrogen	3.58	4.50	3.99			
Chlorine	15.89			15.90	15.79	15.85

These results agree best with those calculated for the formula given above, although it is not impossible that the substance may contain more hydrogen. It is obvious, however, that the formula of the substance cannot be considered as established, until the analytical data have been supported by experiments with some of its derivatives. We shall not at present indulge in any speculations on the constitution of this substance. It crystallizes usually in balls of indistinct little prisms, but occasionally slender short prisms terminated by a single plane at a very sharp angle were observed. Like its mother substance, it has a strong tendency to come down from its solutions in the

form of a varnish. It melts at 164°, and is very soluble in alcohol, mnch more so than the oxide from which it was obtained; easily soluble in acetone, or glacial acetic acid; sparingly soluble in ether, benzol, or chloroform; insoluble in carbonic disulphide, or water. It shows weak acid properties, since it dissolves in a solution of sodic hydrate, and is reprecipitated by an acid. Aniline acts upon it, but we have not yet studied the products. Alcohol seems to be the best solvent for it. The study of this substance will be continued in this Laboratory next year, and we hope the results of this work will not only definitely establish its formula, but also throw much light on the constitution of the body we have called the oxide of dichlordiethoxy-hydroquinone dibenzoate, from which it was obtained.

Dibenzoate of Dichlordiethoxyhydroquinone,
$$C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2.$$

This substance, which was made in order to compare it with the oxide of dichlordiethoxyhydroquinone dibenzoate just described was prepared as follows. The sodium salt of the substituted hydro-quinone was treated with a slight excess of benzoyl chloride, and the product boiled with water to decompose the benzoyl chloride which had not entered into the reaction. After filtering hot the residue was recrystallized from a mixture of alcohol and chloroform until it showed the constant melting point 215°, when it was dried at 100°, and analyzed with the following result : —

0.2000 gram of the substance gave by the method of Carius 0.1202 gram of argentic chloride.

	Calculated for $C_6Cl_2(OC_2H_5)_2(OCOC_6H_5)_2.$	Found.
Chlorine	14.95	14.86

Properties of the Dibenzoate of Dichlordiethoxyhydroquinone. — It crystallizes from a mixture of alcohol and chloroform in long white prisms terminated by two planes meeting at an obtuse angle; these prisms show a tendency to unite longitudinally. It melts at 215°, and is easily soluble in chloroform; soluble in boiling benzol; sparingly soluble in alcohol even when hot, or in glacial acetic acid; insoluble in ether, carbonic disulphide, ligroine, or water. The dilute acids do not act on it even when boiling, nor does strong hydrochloric acid or strong nitric acid produce any visible effect; strong sulphu-ric acid also does not act on it in the cold, but when hot dissolves it, forming a slightly dark-colored solution. Alkalies even in strong boiling solution do not decompose it.

Dichlordimethoxyquinone Dibenzoyldimethylacetal,
$$C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2.$$

This substance was made in the hope that its saponification might throw some additional light on the curious products obtained from the corresponding ethyl compound, and described in the preceding sections. For this purpose 17 grams of the sodium salt of dichlordimethoxy-quinone dimethylhemiacetal were suspended in methyl alcohol, and 20 grams of benzoyl chloride added (this is a little more than the calculated amount), after warming for a short time to finish the reaction, the liquid was allowed to cool, the solid, which had separated, filtered out, and washed first with alcohol and afterward with water. The residue was purified by crystallization from a mixture of alcohol and chloroform until it showed the constant melting point 193°, when it was dried at 100°, and analyzed with the following result: —

0.2052 gram of the substance gave by the method of Carius 0.1163 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OCH_3)_2(OCOC_6H_5)_2.$	Found.
Chlorine	13.95	14.02

The substance crystallizes from a mixture of alcohol and chloroform in several different forms, which however may be produced by the twinning of a single form in different ways. The simplest form observed consisted of rather long plates terminated by two planes at an obtuse angle to each other; these frequently appeared as broad blades in radiating groups, when less well developed. A second very common form was white thick plates, square or nearly so, which showed evidence of twinning, and finally mixed with these were sharp thick rhombic crystals looking like very acute scalenohedra, and showing a line of twinning along the diagonal between the two acute angles. Whether these were different habits of the same form, or indicated that the substance was not homogeneous, mattered little to us, as the saponification with sulphuric acid of specific gravity 1.44 gave a product which was evidently homogeneous, and this was the substance in which we were especially interested. The dichlordimethoxyquinone dibenzoyldimethylacetal is white, and melts at 193°. It is easily soluble in chloroform; soluble in benzol; sparingly soluble in alcohol, ether, glacial acetic acid, or carbonic disulphide; insoluble in water or ligroine. The best solvent for it is a mixture of alcohol and chloroform.

Saponification of Dichlordimethoxyquinone Dibenzoyldimethylacetal.

The substance was boiled with sulphuric acid of specific gravity 1.44, in the manner already described under the corresponding ethyl compound, and the phenomena observed in this case were exactly similar to those presented by the ethyl compound. The product of the reaction was purified by recrystallization from a mixture of chloroform and alcohol until it showed the constant melting point 205°–206°, when it was dried at 100°, and analyzed with the following result : —

0.2071 gram of the substance gave according to the method of Carius 0.1288 gram of argentic chloride.

	Calculated for $C_6Cl_2(OCH_3)_2(OCOC_6H_5)_2O$.	Found.
Chlorine	15.33	15.38

This product therefore corresponds to that obtained by the saponification of the ethyl compound, and this view of its nature is confirmed by the striking similarity between these two substances in crystalline form.

Properties of the Oxide of Dichlordimethoxyhydroquinone Dibenzoate. — It crystallizes from a mixture of alcohol and chloroform in white well formed rhombic prisms, shorter than they are broad, terminated by a very obtuse octahedron and a basal plane forming a very blunt end; the prisms are frequently rendered six-sided by the presence of two basal planes on the acute edges. It melts at 205°–206°, and is readily soluble in chloroform; soluble in glacial acetic acid, or benzol; slightly soluble in alcohol, acetone, or carbonic disulphide; very sparingly soluble in ether; insoluble in water. The best solvent for it is a mixture of alcohol and chloroform.

Dichlordiethoxyquinone Diethylacetaldicarbonic Ester,
$$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2.$$

After we had succeeded in replacing the sodium in the salts of the hemiacetals described in this paper with the benzoyl radical, it seemed of interest to see whether other acid chlorides would act in the same way, and we therefore tried the action of chlorocarbonic ester. Four grams of the sodium salt of dichlordiethoxyquinone diethylhemiacetal suspended in absolute alcohol were mixed with a slight excess of chlorocarbonic ester, and warmed on the steam bath for a few minutes in order to complete the reaction. The solution was filtered while still hot from

the precipitate of sodic chloride, and the filtrate on cooling deposited well formed crystals of the new substance, which was purified by recrystallization from alcohol until it showed the constant melting point 122°–123°, when it was dried, and analyzed with the following result : —

> 0.1866 gram of the substance gave by the method of Carius 0.1075 gram of argentic chloride.

<table>
<tr><td></td><td>Calculated for
$C_6Cl_2(OC_2H_5)_2(OC_2H_5)_2(OCOOC_2H_5)_2$.</td><td>Found.</td></tr>
<tr><td>Chlorine</td><td>14.18</td><td>14.24</td></tr>
</table>

The substance crystallizes in white flat prisms, terminated usually by a single plane at a very sharp angle, which is occasionally modified by a second smaller plane. It melts at 122°–123°, and is readily soluble in alcohol, chloroform, benzol, or acetone; soluble in glacial acetic acid, or carbonic disulphide; slightly soluble in ether; insoluble in water. The best solvent for it is alcohol. In view of the results of the saponification of the corresponding benzoyl compound the decomposition of this substance with sulphuric acid of specific gravity 1.44 promises to be interesting. Unfortunately, it was prepared just before the vacation, so that this work must be postponed until the next college year.

Action of Potassic Phenylate on Dichlordiphenoxyquinone. — Tetraphenoxyquinone, $C_6(OC_6H_5)_4O_2$.

By treating 10 grams of pure dichlordiphenoxyquinone with a little more than two equivalents of potassic phenylate, made by dissolving 4 grams of potassic hydrate and 12 grams of phenol in 150 c.c. of water, tetraphenoxyquinone was formed. In order to complete the reaction it was necessary to boil the dichlordiphenoxyquinone with the potassic phenylate for twenty to thirty minutes. The product formed was then filtered off, and after washing thoroughly with water and alcohol was purified by crystallization from benzol until it gave the constant melting point of 229°–230°. After drying at 100°, the substance gave the following results on analysis : —

> I. 0.2198 gram of the substance gave on combustion 0.6122 gram of carbonic dioxide and 0.0865 gram of water.

<table>
<tr><td></td><td>Calculated for $C_6(OC_6H_5)_4O_2$.</td><td>Found.</td></tr>
<tr><td>Carbon</td><td>75.63</td><td>75.97</td></tr>
<tr><td>Hydrogen</td><td>4.20</td><td>4.37</td></tr>
</table>

This body can also be formed by the action of four equivalents of potassic phenylate in aqueous solution on chloranil, or by the action of sodic phenylate on the dichlordiphenoxyquinone suspended in benzol. In this latter case the sodic phenylate was prepared by dissolving phenol in a rather large volume of benzol, and then adding the required quantity of sodium, which disappeared completely after warming the solution on the steam bath for some time. Neither of these methods gives so good a result as the one described at the beginning of this section. On the other hand, the tetraphenoxyquinone is not formed when the dichlordiphenoxyquinone is treated with sodic phenylate, which has been made by the action of metallic sodium on absolute alcohol mixed with phenol, as in this case the principal product is diethoxydiphenoxyquinone.

Properties of Tetraphenoxyquinone. — It crystallizes from benzol in red prisms which, when well developed, have blunt ends formed by a number of planes or by a single plane at an oblique angle. When smaller they appear as long somewhat shuttle-shaped prisms, radiating from a common centre, but not forming circular groups. It melts at 229°–230°, and is soluble in hot chloroform, boiling acetic anhydride, or boiling benzol; slightly soluble in carbonic disulphide, or boiling glacial acetic acid; very sparingly in warm acetone; insoluble in water, alcohol, ether, or ligroine. The best solvent for it is boiling benzol.

The tetraphenoxyquinone is not easily attacked by reducing agents; sulphurous acid at ordinary temperatures, or in a sealed tube at 100°, has no action on it; hydriodic acid, or a mixture of stannous chloride and hydrochloric acid, reduces it, but the action is very slow; on the other hand, it is easily reduced by glacial acetic acid and zinc dust.

Saponification of Tetraphenoxyquinone.

Toward acid saponifying agents the tetraphenoxyquinone shows a remarkable stability. Sulphuric acid of specific gravity 1.44 has no effect whatever, even after long continued boiling, but hot strong sulphuric acid of specific gravity 1.83 dissolves it, giving a solution from which nothing is precipitated on adding water. This may be due to the formation of a sulphonic acid, but we have not as yet studied the reaction carefully.

A better result was obtained by boiling the tetraphenoxyquinone with a solution of sodic hydrate (one part in four) for about two hours, as it was then completely dissolved, giving a dark purple color to the solution, which on cooling deposited small black crystals of a sodium

salt. The alkaline solution, when poured into an excess of dilute acid, gave a reddish yellow precipitate, which was filtered out, washed with water, and, after purification by recrystallization from alcohol, dried, and analyzed with the following result : —

0.2224 gram of the substance gave on combustion 0.5436 gram of carbonic dioxide and 0.0794 gram of water.

	Calculated for $C_6(OC_6H_5)_2(OH)_2O_2$.	Found.
Carbon	66.68	66.65
Hydrogen	3.70	3.97

The substance was therefore formed from the tetraphenoxyquinone by replacing two of the phenyl radicals by hydrogen, and is the diphenoxyanilic acid.

Properties of Diphenoxyanilic Acid, $C_6(OC_6H_5)_2(OH)_2O_2$. — It forms glistening rather thick plates, either square or in rectangular oblong forms, having a dark reddish brown color like that of ferric citrate; which the substance also resembles in lustre and general appearance. It melts at about 276°, but the melting point is not sharp, as it shows signs of softening even at 270°. If heated somewhat above its melting point, it puffs up filling the capillary tube with a dark liquid. It is soluble in glacial acetic acid; sparingly soluble in alcohol or hot chloroform; insoluble in ether, benzol, carbonic disulphide, or ligroine. It dissolves slightly in boiling water, imparting a pink color to the solution. It has distinct acid properties dissolving in sodic hydrate to form a black crystalline salt, which dissolves in water with a dark purple color. It is not acted on by acids dilute or strong, cold or hot.

Tetraphenoxyhydroquinone, $C_6(OC_6H_5)_4(OH)_2$.

This body was made by reducing the tetraphenoxyquinone with glacial acetic acid and zinc dust. Two grams of the tetraphenoxyquinone were warmed on the steam bath with these reagents until the red color of the original substance had completely disappeared; water was then added, and the precipitated hydroquinone purified by recrystallizing it from alcohol containing a little hydriodic acid to prevent oxidation. On analysis the following results were obtained : —

0.2015 gram of the substance gave on combustion 0.5558 gram of carbonic dioxide and 0.0862 gram of water,

	Calculated for $C_6(OC_6H_5)_4(OH)_2$.	Found.
Carbon	75.32	75.21
Hydrogen	4.60	4.75

Properties of the Tetraphenoxyhydroquinone. — It crystallizes from alcohol in white well developed rather thick rhombic plates, with a very acute angle, which sometimes show sharp notches in the two ends. When seen on the edge the plates seem to be monoclinic, and are often twinned on the basal plane. Larger crystals are apt to have the form of sharp spear-heads. At 210°, it shows signs of decomposition by beginning to turn red. This change of color increases as the temperature rises, until finally it melts at 219°–220° giving a light red liquid, which on cooling solidifies to a red body, probably the quinone. It is readily soluble in acetone ; somewhat more sparingly soluble in ethyl alcohol, methyl alcohol, or chloroform; sparingly soluble in cold glacial acetic acid, more readily in hot; very sparingly soluble in benzol or ether. It is insoluble in water, carbonic disulphide, or ligroine. Alcohol is the best solvent for it.

Diethoxydiphenoxyquinone, $C_6(OC_2H_5)_2(OC_6H_5)_2O_2$.

This substance was obtained in some of our earlier attempts to make tetraphenoxyquinone by treating dichlordiphenoxyquinone with sodic phenylate dissolved in absolute alcohol, 10 grams of dichlordiphenoxyquinone were mixed with two equivalents of sodic phenylate made by treating 1.6 grams of sodium with about 20 c.c. of absolute alcohol and then adding 8 grams of phenol. On the addition of the sodic phenylate the dichlordiphenoxyquinone became dark-colored, and a very black tarry solution was obtained, which after standing for two hours was separated by filtration from the sodic chloride formed ; water was then added to the filtrate, which precipitated an oily black liquid. In order to purify this liquid it was repeatedly washed with water by decantation, and then dissolved in alcohol, from which beautiful silky orange-yellow needles were obtained, and these were recrystallized from alcohol until they showed the constant melting point 128°, when after drying in a desiccator they gave the following results on analysis : —

0.2104 gram of the substance gave on combustion 0.5324 gram of carbonic dioxide and 0.1004 gram of water.

	Calculated for $C_6(OC_2H_5)_2(OC_6H_5)_2O_2$.	Found.
Carbon	69.47	69.01
Hydrogen	5.26	5.30

The yield is small. The diethoxydiphenoxyquinone crystallizes in long silky orange-yellow slender needles arranged in radiating groups. It melts at 128°, and is readily soluble in alcohol or chloroform; soluble in carbonic disulphide or benzol; sparingly soluble in ether or glacial acetic acid; insoluble in ligroine or water. The best solvent for it is alcohol.

Action of Sodic Methylate on Tetraphenoxyquinone. (*Dimethoxy-diphenoxyquinone,* $C_6(OCH_3)_2(OC_6H_5)_2O_2$.)

When 5 grams of tetraphenoxyquinone were treated with a solution of six equivalents of sodic methylate in methyl alcohol, it dissolved to a colorless liquid, which on standing deposited a quantity of nearly white needles. These were filtered off, and after washing with a little methyl alcohol treated with water rendered alkaline by sodic hydrate, when a portion of the substance was dissolved, and a yellow crystalline body was left as an insoluble residue. This latter substance was purified by crystallization from a mixture of benzol and alcohol until it showed the constant melting point 171°, when it was dried at 100°, and analyzed with the following result : —

0.2043 gram of the substance gave on combustion 0.5068 gram of carbonic dioxide and 0.0862 gram of water.

	Calculated for $C_6(OCH_3)_2(OC_6H_5)_2O_2$.	Found.
Carbon	68.19	67.66
Hydrogen	4.55	4.69

The substance is therefore dimethoxydiphenoxyquinone formed by the replacement of two of the phenyl by methyl radicals.

Properties of Dimethoxydiphenoxyquinone. — It crystallizes from a mixture of alcohol and benzol in beautiful long golden-yellow needles, which under the microscope are seen to be slender prisms arranged in radiating groups. The terminations of these prisms consist of one principal plane, sometimes at a right angle, sometimes at an oblique angle to the sides ; in this latter case, when the crystals are large enough, small modifying planes are also seen. It melts at 171°, and is readily soluble in chloroform ; soluble in ethyl or methyl alcohol, benzol, or glacial acetic acid ; sparingly soluble in ether or carbonic disulphide ; insoluble in ligroine or water. It is reduced by zinc and glacial acetic acid to a colorless hydroquinone.

It dissolves apparently with decomposition in a dilute solution of sodic hydrate, and from this solution dilute sulphuric acid precipitates

a non-crystalline body insoluble in water, but soluble in sodic hydrate with a fine purple color.   We have not had time as yet to study this substance more carefully.

When the yellow dimethoxydiphenoxyquinone was mixed with a solution of sodic methylate in methyl alcohol, and the mixture stirred vigorously, the yellow solid disappeared, and a white crystalline sodium salt was precipitated.   This precipitate dissolved in water without residue, and from the solution the addition of a dilute acid threw down a white amorphous solid, which decomposed almost immediately into a yellow substance probably dimethoxydiphenoxy-quinone.   These observations show that in this case a hemiacetal was formed, but a much less stable one than that obtained from the quinones containing chlorine.   It seems, therefore, that the stability of the hemiacetals depends on the number and strength of the negative radicals attached to the quinone ring.

Action of Sodic Phenylate on Bromanil.

In order to study this action 2 grams of bromanil, prepared accord-ing to Stenhouse,* were treated with an alcoholic solution† of sodic phenylate made by acting on 0.3 gram of sodium with absolute alcohol and then adding 3 grams of phenol.   The bromanil began to turn red as soon as the phenylate was added, but it was necessary to warm the mixture in order to make the reaction complete.   After this the solution was filtered, and the solid remaining on the filter, after thorough washing with water and alcohol, was purified by crystalliza-tion from benzol until it showed the constant melting point 266°–267°, when it was dried at 100° and analyzed with the following result : —

> 0.1677 gram of the substance gave, according to the method of Carius, 0.1393 gram of argentic bromide.

	Calculated for $C_6Br_2(OC_6H_5)_2O_2$	Found.
Bromine	35.56	35.36

The substance is, therefore, dibromdiphenoxyquinone, and it is to be observed that bromanil behaves differently from chloranil with this

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* Ann. Chem., Suppl. VIII. 13.

† This experiment was tried early in our work, before we had found that an aqueous solution of the sodic phenylate acted better on chloranil than the same reagent dissolved in alcohol.   If we were to repeat this preparation, therefore, we should use a solution in water instead of in alcohol.

alcoholic solution of sodic phenylate, for the latter lost all four of its atoms of chlorine, two being replaced by phenoxy and two by ethoxy groups. The bromanil, on the other hand, behaves with the alcoholic solution of sodic phenylate as chloranil does with an aqueous solution of this reagent, the action consisting in the replacement of two atoms of halogen by two phenoxy groups.

Properties of Dibromdiphenoxyquinone. — It crystallizes from benzol in rather short orange-red needles with blunt points, melting at 266°–267°. It is very slightly soluble in alcohol even when hot; insoluble in ether or ligroine, or in water whether cold or hot; sparingly soluble in carbonic disulphide or boiling benzol, and only very slightly soluble in cold benzol ; more soluble in chloroform ; freely soluble in hot glacial acetic acid, slightly in cold. The three strong acids have no visible effect upon it. By the action of glacial acetic acid and zinc dust it is reduced to a colorless hydroquinone. It reacts easily with sodic methylate, ethylate, or phenylate, and also with sodium malonic ester, or aniline, but we have studied only its action with sodic methylate.

Dibromdimethoxyquinone Dimethylhemiacetal,
$C_6Br_2(OCH_3)_2(OH)_2(OCH_3)_2.$
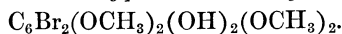
This body was formed by treating 1.4 grams of dibromdiphenoxy-quinone with a solution of rather less than four equivalents of sodic methylate in methyl alcohol, which was made by the action of a little methyl alcohol on 0.3 gram of metallic sodium. When the sodic methylate was first added, there was no apparent action, but after warming on the steam-bath for a few minutes a white crystalline sodium salt separated. The salt was filtered out, washed with a little methyl alcohol, dissolved in water, filtered again, and then dilute sulphuric acid added in excess, which gave a bulky white precipitate. This was filtered off, washed with water, alcohol, and ether, and then dried for a short time over sulphuric acid and paraffine. The product was analyzed with the following results : —

0.2047 gram of the substance gave by the method of Carius 0.1966 gram of argentic bromide.

	Calculated for $C_6Br_2(OCH_3)_2(OH)_2(OCH_3)_2.$	Found.
Bromine	41.03	40.88

The dibromdimethoxyquinone dimethylhemiacetal is a white amorphous solid insoluble in all the common solvents. It melts at 178°–

188°, at the same time changing to a red substance, probably dibrom-dimethoxyquinone. This change can also be produced by treatment with dilute sulphuric acid, or dilute hydrochloric acid. From this description of the preparation and properties of this hemiacetal it is evident that the action of sodic methylate on dibromdiphenoxyquinone is similar in every respect to the action of this reagent on the corresponding compound containing chlorine.

Action of Potassic Phenylate on Trichlorquinone.

By treating 5 grams of trichlorquinone suspended in water with two equivalents of potassic phenylate, made from 2.7 grams of potassic hydrate and 8 grams of phenol, a red semi-liquid substance was formed. After the mixture had been heated on the steam bath for twenty minutes in order to complete the reaction, the supernatant liquid was poured off, and the pasty residue washed with water by decantation, and then warmed with alcohol, which converted it into a crystalline solid. These crystals were then separated by filtration, washed thoroughly with cold alcohol, and recrystallized from alcohol containing a small amount of benzol until they showed the constant melting point 169°–170°, when they were dried at 100°, and analyzed with the following results : —

I. 0.1888 gram of the substance gave by the method of Carius 0.0818
    gram of argentic chloride.
II. 0.1913 gram gave 0.0832 gram of argentic chloride.

	Calculated for $C_6HCl(OC_6H_5)_2O_2$.	Found.	
		I.	II.
Chlorine	10.87	10.71	10.75

Properties of Monochlordiphenoxyquinone. — It crystallizes from alcohol in long, slender, pointed oval blades arranged in irregular groups, — a very characteristic habit of crystallization. It has an orange color, with a slight brownish tinge, and melts at 169°–170°. It is easily soluble in benzol or chloroform ; difficultly soluble in alcohol ; slightly soluble in carbonic disulphide ; insoluble in water, ether, or ligroine. It is easily reduced to a colorless hydroquinone by glacial acetic acid and zinc dust.

To see whether it would form a hemiacetal 0.5 gram of the monochlordiphenoxyquinone was treated with the sodic methylate made by acting on 0.3 gram of metallic sodium with a few cubic centimeters of methyl alcohol. The quinone dissolved in the cold, but, even when allowed to stand for some time and stirred vigorously, no precipitate

of a sodium salt was formed. When, however, it was warmed for a few minutes, a heavy white precipitate was deposited, which, after being washed with a little methyl alcohol, dissolved completely in water, giving a clear solution. The addition of an acid to this solution produced a turbidity, which soon developed into a white precipitate, undoubtedly the hemiacetal, but this passes so easily into a red quinone derivative that we have not attempted to analyze it, especially as its properties leave no doubt as to its nature. It follows from these observations that the stability of the hemiacetals is increased by the number of negative radicals, such as chlorine atoms, present.

Action of Sodic Ethylate on Quinone.

Although the results described in the last section made it probable that the hemiacetal derived from quinone itself would be very unstable, we have tried some experiments on the action of sodic ethylate on quinone $(C_6H_4O_2)$, and think it best to give a preliminary account of them here, in spite of the fact that they have not led as yet to any definite result. They have, however, proved that sodic ethylate acts on quinone, but have by no means convinced us that the product is a hemiacetal. On treating quinone dissolved in ether with an alcoholic solution of sodic ethylate, a heavy flocculent dark green precipitate is formed, which is insoluble in ether, but dissolves in alcohol or water with decomposition. This precipitate does not seem to be homogeneous, as by fractional precipitation products were obtained unlike in color, and also in their composition, as shown by analysis; moreover its study is rendered difficult by the fact that it takes fire spontaneously when dried at ordinary temperatures in the air; if, however, it is dried in an atmosphere of hydrogen, it can be exposed to the air without taking fire at ordinary temperatures, but, if warmed to 40°, it begins to glow, and burns like tinder. Before studying this rather unmanageable substance further, we tried to get some idea of the way in which the reaction ran by a quantitative study of it, based upon the fact that all the quinone can be removed from its ethereal solution by the sodic ethylate.

In the first trial, it was found that one gram of quinone required 0.2352 gram of sodium for complete precipitation.

In the second trial, one gram of quinone required 0.2460 gram of sodium.

In the third trial, 3 grams of quinone required 0.6 gram of sodium.

These results indicate that each molecule of quinone acts with only one molecule of sodic ethylate, as the amount of sodium needed in this

case for one gram of quinone is 0.213 gram, and the observed results come as near to this number as could be expected, when the roughness of the method is considered. This conclusion is confirmed by the yield of the salt obtained from 3 grams of quinone, which was 4.7 grams, whereas, if only one molecule of sodic ethylate had been added to each molecule of the quinone, the yield should have been 4.9 grams. The study of other parts of this research has occupied our time so completely that we have been unable to do more on this division of the subject, but we hope that this work can be taken up again in this Laboratory at an early date.

Experiments on Phenoquinone.

It has been suggested in the introduction that phenoquinone and quinhydrone may be hemiacetals similar to those studied in this paper. In that case phenoquinone should contain two hydroxyl groups, and form salts. Accordingly, we have tried to obtain a salt of it, although the chances of success were not great as Wichelhaus [*] has stated that phenoquinone forms no salts, but is decomposed by alkalies. Still we thought that possibly by using sodic ethylate in insufficient quantity we might succeed, as the replacement of the hydrogen by the metal might take place in preference to the decomposition of the phenoquinone, especially as Wichelhaus also states that it gives a blue color with alkalies. We proceeded as follows. One gram of phenoquinone [†] was dissolved in ether, and treated with an alcoholic solution of the sodic ethylate made from 0.1 gram of sodium ; as 0.154 gram of sodium would be required for two atoms of sodium to each molecule of phenoquinone, there was a considerable excess of this latter substance. As soon as the sodic ethylate was added, a heavy flocculent dark green precipitate was formed, which was filtered out, washed thoroughly with ether, and dried over sulphuric acid and paraffine. We hoped at first that this was the salt of phenoquinone, and three sodium determinations seemed to confirm this idea, as they gave 13.14, 13.41, and 14.31 per cent of sodium, which is not far from the number calculated for a sodium salt of phenoquinone, since that is 13.52 per

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[*] Ber. d. ch. G., V. 248.

[†] The phenoquinone was made by adding one equivalent of quinone dissolved in hot ligroine to two equivalents of phenol dissolved in a small quantity of the same solvent. The mixed solutions were warmed for a few minutes, and then on cooling beautiful red crystals separated, which were purified by recrystallization from alcohol.

cent of sodium; but the study of the ethereal filtrate from the salt
threw a great deal of doubt on this conclusion, since it contained a
large amount of phenol. We think it more probable, therefore, that
the sodic ethylate decomposed the phenoquinone into quinone and
phenol, and that the green salt was then formed by the action of the
sodic ethylate upon the quinone, the action being the same as that
described in the last section. This inference is strengthened by the
marked resemblance in appearance between the salts obtained in these
two cases, and also by the study of the properties of the salt made
from the phenoquinone, since it dissolved completely in water, forming
a dirty green solution, and undoubtedly suffering partial decomposi-
tion, as ether extracted from this solution colorless crystals of hydro-
quinone recognized by their melting point of 169°. The addition of
an acid to this solution gave no precipitate, and upon shaking out the
acidified liquid with ether, nothing was extracted but hydroquinone.
If the substance had been the desired salt of phenoquinone, phenol
should have been obtained from this filtrate. Although these experi-
ments tell against the formation of salts of phenoquinone, we do not
consider them absolutely final, but the study of the action of alkalies
on phenoquinone under other conditions will be continued in this
Laboratory during the coming college year.

As we had not succeeded in making a salt of phenoquinone we next
turned our attention to the action of sodic phenylate on quinone, as,
if the phenoquinone is a hemiacetal, this should act as well as free
phenol, whereas according to the other theories of the constitution of
phenoquinone, it is hard to see how there should be any action in this
case. Sodic phenylate was made by warming the proper amount of
metallic sodium with a solution of phenol in benzol until the sodium
had entirely disappeared. As the benzol cooled, the white crystalline
sodic phenylate separated abundantly, and, after filtering, any free
phenol was removed by washing with cold benzol. Upon adding the
solid sodic phenylate to a solution of quinone in absolute ether a dark
red crystalline substance looking like phenoquinone was formed.
After evaporating off the ether slowly, the residue dissolved easily in
water with a slight green color, and acids precipitated from this
aqueous solution a small amount of a dark reddish solid. The ethereal
solution showed a tendency to turn green round the edges during the
evaporation which may perhaps have been due to the action of the
moisture in the air. If benzol was used to dissolve the quinone in-
stead of ether, a pink substance was formed, which changes to a dark
green body when warmed. With ligroine as the solvent, a dark green

precipitate was obtained at first. Unfortunately, this work was undertaken at the very end of the term, so that a more careful study of these products must be postponed until next year, but these preliminary experiments show that sodic phenylate does combine with quinone, and therefore lend a certain amount of countenance to our suggestion that phenoquinone is a hemiacetal.